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The Use of Radioisotopes in the U.S.S.R.*

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NATURAL radioisotopes were first used in the Soviet Union shortly after the 1917 Revolution. Natural radioactive elements were used by E. S. LONDON and others for the treatment of cancer, by VERNADSKY, KHLONIN, STARIK and others[1] to determine the age of minerals, and by SNITSYN in analytical chemistry.[2] The use of artificial radioisotopes in the U.S.S.R. started directly after the publication, in 1934, of a paper by the two Joliot–Curies. The first paper on the use of artificial radioisotopes in chemical research was published in the U.S.S.R. in 1935.[3]

After the Second World War, the production of radioactive isotopes began in the U.S.S.R. by the irradiation of material in cyclotrons and nuclear reactors; in some cases the irradiated material consisted of a single isotope, to prevent the formation of undesirable impurities. For example, among the isotopes obtained by irradiation are, Fe^{59}, Fe^{55}, Ca^{45} and Sn^{123}. Other isotopes, such as Sr^{90}, Y^{90}, Ce^{144}, Cs^{137} and Pm^{147} were extracted from fission products.

The growth of the radioisotope industry in the U.S.S.R. is illustrated in Fig. 1, where is shown the increase in the production of C^{14} and Co^{60} over the period 1953–1957, and the number of consignments dispatched to China, Eastern Europe, and throughout the Soviet Union. In 1957, 75 different radioactive isotopes, and a large number of compounds labelled with radioisotopes, were available in the U.S.S.R.

As the production of isotopes and measuring equipment expanded, so did the number of laboratories using radioisotopes in scientific and technological research. Specialized laboratories were set up for the use of radioisotopes in chemistry, industry, biology, agriculture and medicine, and many laboratories in scientific establishments and universities in Moscow, Leningrad, Kiev, Gorky, Kharkov and Minsk now use radioisotopes. After 1949 a number of laboratories in scientific institutes and industrial concerns in Uzbekistan, Kazakhstan, Latvia and other Soviet Republics began to use labelled atoms. An important step in expanding the use of radioisotopes was the organization by the Institutes of Physics, Physical Chemistry, and Biophysics of courses in isotope techniques for engineers, chemists, biologists and medical workers.

To describe all the varied applications of radioisotopes, or even to list in full the names of those who have made important advances in this field, would far exceed the scope of this paper. The present account will, therefore be limited to some of the most important work in chemistry, technology, biology, medicine and agriculture.

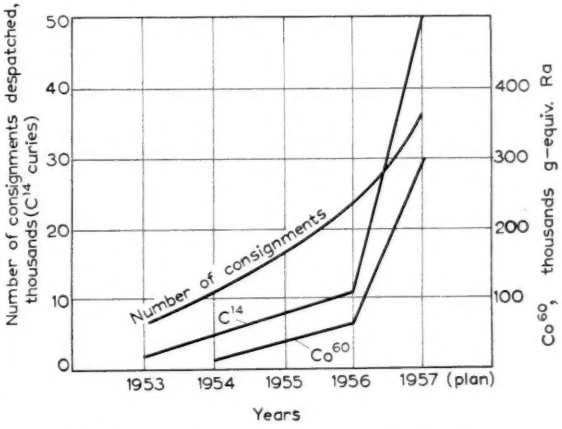

FIG. 1.—The growth of radioisotope production in the U.S.S.R.

* Translated by L. C. RONSON from *Atomnaya Energiya* **3**, No. 11, 465 (1957).

RADIOISOTOPES IN CHEMISTRY

Artificial radioisotopes were used in the U.S.S.R. in chemical research earlier than in other countries. Papers published during 1935–1938 marked the beginning of a long series of experiments on isotope exchanges in halides, and on the mechanism of catalytic processes.[3,4] Before the Second World War, chemical investigations employing artificial radioisotopes were centred in Leningrad at the Radium Institute, the Institute of Chemical Physics, and at Leningrad University. After the war the scope and range of these investigations were considerably expanded.

Inorganic chemistry

Systematic researches have been carried out for many years on the mechanism of isotope exchange in complex platinum compounds.[5] The ease of exchange in the case of the attached groups compared to that of the central atoms, and its variation with an increase in their thermodynamic bond strength, were confirmed by various investigations abroad.

The isotopic exchange of bromine between the bromides of a large number of elements and elementary bromine, and the exchange of sulphur with polythionates was investigated in detail by numerous authors.[6,7] Brodsky, on the basis both of his own results and of data given in the literature, concluded that isotope exchange reactions may proceed either by a dissociation or by an association mechanism. The isotope I^{131} was used to prove the equivalence of the iodine atoms in the HgI_4^{2-} anion. The equivalence of the bromine atoms in $HgBr_4^{2-}$ and also in $TlBr_3$, PBr_3 and PBr_5 was established by using Br^{82}.[8] S^{35} was used to investigate the mechanism of formation of thiosulphate in the reaction of H_2S, SO_2 and NaOH. It was shown that the central sulphur atom in thiosulphate is formed from SO_2, and the attached atom partly from H_2S (two thirds) and partly from SO_2 (one third).[9]

Work on the diffusion rates of the constituents of inorganic crystalline salts,[10] showed that the diffusion rates of cation and anion can vary by several orders of magnitude. Extension of this work led to the development of a theory of exchange by diffusion in the systems solid–gas, solid–liquid and solid solution.

Work on the self-diffusion of iron in binary alloys,[11] showed that the diffusion rate decreases rapidly with the formation of chemical compounds, and a new method of physicochemical analysis was developed based on the variation of diffusion coefficient with alloy composition. A discontinuity in the diffusion coefficient corresponds to the formation of a chemical compound in the alloy.

Soviet workers have obtained important results in analytical chemistry by using radioisotope techniques. The two main advantages of radioactive tracer techniques are their high sensitivity and the possibility of making measurements by non-destructive methods. Radio-tracer methods have been used to determine the optimum conditions for analysing chemically similar materials. For example, radio-bromine and radio-iodine were used to show that separation of iodides and bromides by nitric acid oxidation was quantitative;[12] the use of Ca^{45} showed that the oxalate method of separating calcium and magnesium was liable to gross error;[13] Sr^{90} and Ba^{140} were used to determine the optimum conditions for separation of these elements by the chromate method.[14]

Many authors have investigated co-precipitation in gravimetric analysis with inorganic and organic reagents.[15] A method employing adsorption on carbon was developed for the separation and purification of radioactive isotopes. A number of papers have been published on the study of extraction using tracer techniques.[15]

Radioactive isotopes have been widely used for studying the separation of salt and gaseous mixtures by chromatography.[16] Radioactivation methods have been used to determine small amounts of rare-earth impurities in various metals and graphite, and

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also to determine copper, antimony, molybdenum and zinc in germanium and germanium oxide.[17] A number of new applications of the isotope dilution method have been developed; for example, for the determination of methyl alcohol, ethyl alcohol and propyl alcohol in mixtures.[18]

Physical chemistry

Radioisotopes have been widely used in the Soviet Union for research in physical chemistry. Radio-tracer methods have been successfully applied to determine the vapour-pressure of metals, salt and oxides in pure form, and in their mixtures.[19] The liquid–vapour equilibrium of dilute solutions of acetic acid in water, ethyl acetate in carbon disulphide and a number of other binary systems, has been studied. A new rapid method of determining solubility was developed, and the solubilities of a large number of salts have been determined.[20]

Much important theoretical and experimental work has been done on isotope separation.[21,22]

In the field of chemical reaction kinetics Soviet workers have developed new methods for the use of radioactive isotopes to study the mechanisms of homogeneous and heterogeneous reactions. Isotope methods have been developed[23] for studying reaction kinetics, including determination of the formation sequence of intermediate products in complex reactions, the formation rate, the losses, and the order of the reactions. These methods are widely employed, in particular in the Institutes of Chemical Physics, Physical Chemistry and Organic Chemistry, and in the Universities of Moscow and Saratov.

A deuterium exchange method has been developed and applied to the identification of radicals in hydrocarbon cracking reactions.[24] A new method was developed for the differentiation between molecular-, radical-, and chain-reactions by comparing their reaction rates in mixtures not in equilibrium, and also in thermodynamic equilibrium.[25] Br^{82} and I^{131} have been used to study isotope exchange rates for halogen atoms and other ions. The investigation showed that the variations of structure which accelerate the ion-molecular exchange reaction, slow down the isotope exchange occurring by the radical or chain mechanism.[26] It was shown that an increase of pressure accelerates isotope exchange reactions in alcoholic solutions, but retards the same reactions when ketones are used as solvents.[27]

Very interesting isotopic effects have been observed in the reduction of oxides of various metals with tritium.[28]

Many methods using stable and active isotopes have been suggested and applied to study surface inhomogeneities,[29] in order to differentiate between the effect of mutual repulsion and surface inhomogeneity on the nature of adsorption isotherms, and on adsorption and desorption processes.[30]

Solid reaction kinetics, such as in the vulcanization of rubber, have been studied by observing the rate of diffusion of labelled substances.[31]

Radioactive tracer methods have been used to establish the equivalence of N—C bonds in the tetramethylammonium ion[32] and of the bonds of sulphur and other atoms in many compounds.[7] Tracer techniques have been used to measure current density in conditions in which a reversible potential exists between the metal and its ions in a solution.[33]

Organic chemistry

Stable and active isotopes have been very widely applied to study reaction mechanisms in organic chemistry. The positions for formation and rupture of bonds during esterification, hydrolysis, and the reduction of aldehydes, have been studied. The phenomenon of hydrogen migration was discovered; the regrouping of allyl ethers, phenols, the Beckman rearrangement and several tautomeric changes have been investigated.[8]

Using a heavy isotope of oxygen, a systematic error was discovered in what has been long considered a classic paper by POPYANI, and a new method was developed

to locate the positions of bond rupture during the saponification of complex ethers; this was used to show that various bonds may break during the reaction depending on the structure of the acid and alcohol, and on the nature of the saponifying agent.[34] The hydrogen exchange of a number of organic compounds in ammonia and in liquid HBr was studied in some detail, and it was shown that the exchange capability of different hydrogen atoms may be appreciably dependent on the solvent.[35] Radiotracers have been used at the Gorky Institute of Chemistry[36] to study the dissociation of phosphorus pentaphenyl and the reaction mechanism of various metal organic compounds. Hg^{203} was used[37] to show that a reversal of the configuration occurs during the "electrophilic substitution" with participation of one of the carbon atom bonds.

Radioactive tracers are widely used for process control in the chemical industry.[38] By adding to ethane a small quantity of methane labelled with C^{14}, a detailed study was made of the products of thermal decomposition of ethane, and constants for some of the reactions taking place were deduced.[39]

A number of papers have described the role played by the catalyst in catalytic oxidation reactions. Radioisotopes have been used to measure the surface area of various materials in the cement industry, of porous solids by the emanation method, and for similar problems.[40] The structure of concrete[41] has been studied using Ca^{45} etc.

RADIOISOTOPES IN TECHNOLOGY

Radioactive isotopes have found many applications in technology and the technical sciences, such as: metallurgy, metallography, mechanical engineering, instrument design, heat technology, mechanics, and ore processing. Isotopes are used both as sources of radiation, and as tracers.

The advent of a cheap source of γ-rays, Co^{60}, made possible a large scale development of inspection methods for metallic components. The high penetrating power of the γ-radiation from Co^{60} allows flaws to be found in castings up to 30 cm in thickness, whereas X-ray examination of steel of thickness greater than 8 cm is very difficult. At present Co^{60} is used for quality control in the manufacture of aircraft and pressure vessels, and metallurgical, engineering and chemical plants.[42–45] Other isotopes with softer radiations such as Ir^{190}, Cs^{137}, Tm^{170} are also used extensively for the examination of smaller thicknesses of metal. In addition to photographic methods, ionization techniques of flaw detection, developed at the Metal Physics Institute in the Uralian Branch of the Academy of Sciences, at the Heavy Metallurgy Central Scientific Research Institute, and in other laboratories, are widely used since they permit continuous inspection of production—for instance of welding seams—without incurring heavy expenditure on X-ray films. In these methods the radiation is recorded by γ-counters.[45,46]

Radioisotopes are widely employed for making process control measurements.[47] The absorption and scattering of radiation is used to determine sheet and strip thickness during rolling, tube wall thickness, the thickness of surface coatings, the density of materials, the levels of liquids and granular substances in closed vessels, for counting articles on a conveyor belt, etc. For example, level gauges are used for the automatic control of liquid metal levels in continuous steel casting. Great economic advantages result from the application of radioactive isotopes to production processes.

Many Institutes have played an important part in the development of equipment using isotopes, in particular the Central Automation Laboratory, the Academy of Sciences Physical Institute, the Latvian Academy of Sciences Physical Institute, the Metal Physics Institute in the Uralian Branch of the Academy of Sciences, the

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Heavy Metallurgy Central Scientific Research Institute, the Academy of Sciences Institutes of Automation and Telemechanics and various others.

The interaction between nuclear radiation and matter is widely used in mineral prospecting and ore processing. Radiation sources placed in a bore hole give scattered radiation which can be detected by counters, and which depends on the density and composition of the strata. This method has been developed and tested in a number of coal fields in the Soviet Union.[73] Radioactivity methods are used on a large scale in oil prospecting[53,56–58] to study the geological structure in bore holes. A neutron source is placed in the bore hole and γ-radiation emitted in neutron capture is detected, and hence strata containing hydrogen are distinguished. Oil-bearing and water-bearing shales are differentiated by means of γ-spectrometers. These methods were developed by the Academy of Sciences Petroleum Institute, the Central Petroleum Scientific Research Institute of Geophysical Exploration, the Gubkina Petroleum Institute, the Academy of Sciences Mining and Geological Institute, and others.[57,58]

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Tracer techniques are used on a large scale in the metallurgical industry.[48–55] The Metal Physics Institute, The Heavy Metallurgy Central Scientific Research Institute, the Academy of Sciences Metallurgical Institute, the Kuznetsky Laboratory of the "Azovstal" Metallurgical Combine of the Stalin Metallurgical Works, and the Nova-Tulsk Metallurgical Works, were principally responsible for the introduction of these methods.

Two aspects of blast furnace operation have been studied: the wear of the refractory lining in the hearth and shaft of the furnace, and the movement of the charge and gases in the furnace.[48] The burning out of the refractory lining has been studied in several works by distributing radioactive sources in different parts of the refractory lining during a major furnace overhaul. During operation of the furnace all the pig and slag leaving the furnace were monitored; radioactivity in metal or slag specimens showed burning of the refractory lining in the region of a source. To measure the rate of descent of the charge, pieces of ore, coke or limestone were labelled; the passage of these pieces through a particular level in the furnace was recorded by counters in water-cooled tubes.[49] The transit time of the furnace gases was measured by adding radon to the blast air, and subsequently recording the activity at the furnace mouth. The results of these investigations were used to improve blast furnace design.

In the steel industry, investigations have been made of the thermodynamics of the distribution of phosphorus, sulphur, chromium, molybdenum and tungsten between the iron and slags of various compositions, principally by the Heavy Metallurgy Central Scientific Research Institute. Distribution coefficients of these elements between iron and slag were first determined as a function of the steel and slag compositions and of their temperature, by measuring the radioactivity of samples of the metal and slag in equilibrium. Radioactive isotopes have been used to study the thermodynamics of solutions of sulphur, phosphorus, chromium, silicon and other elements in liquid iron. Such investigations are conducted either by measuring the partial vapour-pressures of the elements over liquid iron, or by a new method based on measuring the radioactivity of the refractories in contact with molten iron containing the element under study.

Radioactive tracer methods are particularly useful for studying the kinetics of the transfer of phosphorus and sulphur from the metal to the slag, which is of great importance for developing methods of producing grey iron and steel with very low concentrations of these undesirable impurities. Kinetic equations have been established describing dephosphorizing and desulphurizing processes for cast iron and steel, and explaining the factors determining the rate of purification of the metal from these impurities.[32] With the aid of S^{35}, the kinetics of desulphurization in electric arc furnaces have been studied.

In order to determine the process limiting

the rate of exchange of iron between metal and slag, the kinetics of the exchange process were investigated under equilibrium conditions by using Fe^{59}. It was found that the slowest step in the exchange reaction between slag and the liquid metal is diffusion in the slag phase, whilst with stirring, it is the mass transfer in this phase. Study of the exchange and distribution of iron between the slag and the steel under works conditions showed that the rate of exchange was limited by a diffusion process. An investigation of the tungsten distribution between the metal, the slag and the gaseous phase was made at the Kirov Works.

Investigations using Ag^{110} at the Chelyabinsk Metallurgical Works showed that wastage during steel pouring was caused principally by the presence of metal crusts, (i.e. stratification and skin formation) and demonstrated the necessity of developing improved methods.

Using radioisotopes, methods were developed for determining ion transport numbers in mixtures of molten oxides, based on the measurement of very small concentration changes in the melt caused by the passage of a small electric current. It was found that in liquid silicates and phosphates the electric current is carried solely by cations. Measurements of cation transport numbers in melts with two cations allowed determination of relative cation mobility.

One of the most important problems in the metallurgy of high grade steels is the production of steel containing a minimum of non-metallic inclusions. For this purpose it is essential to determine the sources from which non-metallic impurities enter during the melting, casting, and pouring of liquid steel. To study this problem, Ca^{45} was used at a number of steel works to label the liners of the steel pouring ladles, the channels, the siphon supply ducts, and the slag. Subsequent separation of the inclusions from the finished steel, and measurement of the radioactivity, gave information on the sources of contamination. A study of the nature of slag inclusions in bubbling steel showed that these are formed both by entrapping slag floating on the metal surface, and by erosion of the siphon ducts. Suitable techniques were developed by which this fault was appreciably reduced.

Study of the hydrodynamic state of the liquid phases present in the crucible in the Martin furnace is important since it is directly related to heat exchange in the steel crucible, the floating up of non-metallic inclusions, the solution of alloying additions, and de-gassing. These processes were previously studied only by indirect methods, but now, in a number of steel works Co^{60} has been used as a radioactive indicator to study the stirring of liquid steel, since under molten conditions it is completely retained in the metallic phase. The rate of movement of the metal was determined by measuring the radioactivity of metal samples taken from the surface. The results showed that when the oxidation rate of the carbon is high the movement of the metal is turbulent. The isotope dilution method has been used to determine the melting rate of scrap and also the rate of slag formation in Martin furnaces.[51] It was found that the rate of melting is proportional to the weight of solid scrap, while the rate of slag formation is proportional to the weight of limestone to the power 2/3. At the Magnitogorsk Metallurgical Combine, investigations were carried out on the effect of altering the order of loading the materials in a Martin furnace on the speed of melting.

Radioisotopes were used to study the kinetics of the crystallization of steel in moulds in order to determine the actual speed of movement of the solid phase in the solidifying steel, and to determine the effect of crystallization on the distribution of elements in the casting. The positions of the solid phase boundaries were found by successively adding P^{32} and S^{35} which dissolve in steel, and which were introduced during its cooling in the mould.

Recently work has been started dealing with the use of radioactive isotopes for rapid analysis and for checking the accuracy of analytical methods. A rapid method was developed at the "Azovstal" Works to determine the phosphorus pentoxide in slags

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during the phosphorus reduction, based on the addition of a small amount of P^{32} to the grey iron. This method requires only very small quantities of P^{32} (about 0·04–0·05 μc per ton of metal), since a large sample of slag is used, the activity being measured with four counters connected in parallel. A similar method has been developed for very rapid determinations of phosphorus in the metal during the development of a new technique of converter reduction of Martin iron.

Many investigations using radioisotopes have been carried out to study phenomena in metals and alloys in the solid state. Using labelled atoms, the rate of displacement of atoms amongst similar atoms (self-diffusion) and its dependence on temperature have been studied. The study of self-diffusion and diffusion is of special importance for a deeper understanding of the nature of interatomic bonds, phase transformations, and processes taking place in metals and alloys under load at high temperatures. Artificial radioactive isotopes were first employed for this purpose in the Soviet Union where as long ago as 1937 radioisotopes were used to investigate self-diffusion in gold.[59] Much research has been devoted to the development of methods for measuring diffusion coefficients by radioactive tracer methods, and this has yielded a large amount of valuable data on self-diffusion and diffusion in metals and alloys. For example, it has been found that alloying elements may have an appreciable effect on the self-diffusion of the solute metal atoms.[53,60–62] Such information is important for the understanding of processes taking place in alloys at high temperatures, for developing a theory of alloying, and for the development of new alloys.

Radioisotope methods have shown the effect of internal metal grain structure in self-diffusion and diffusion processes. These studies have led to an understanding of the effect of phase transformations on the properties of the alloys at elevated temperatures,[62] and also of the diffusion mechanism.[63]

Microradiography is used to study inhomogeneities in the macro- and micro-structure of metals and alloys and diffusion along grain boundaries. Microradiographic investigations of the distribution of elements in alloys and of grain boundary diffusion are of special interest in the study of processes related to the failure of metallic components.[64]

Tracer methods have been used to extend the investigations of the vapour-pressure of metals and alloys to the study of the thermodynamic characteristics, and the nature of the interaction of atoms of metals and alloys by the Moscow Steel Institute, the Heavy Metallurgy Central Scientific Research Institute, and the U.S.S.R. Academy of Sciences Metallurgical Institute.[61,65–67]

Radioactive tracers may be used to label different cations to determine transfer numbers during the passage of electric current, for research on the electronic structure of solids.

In the field of mechanical engineering, radioactive isotopes have been used to investigate friction and wear processes.[73] By their use it was possible to study the effect on the rate of engine wear of the nature of the lubricant and fuel, and of the engine load and speed. The mechanism underlying the anti-corrosive action of various engine lubricant additions has also been studied[68,69] (see Figs. 2 and 3).

The use of radioisotopes to study the wear of cutting tools has reduced the working time and the material required, and helped to assure optimum cutting conditions.[70]

At the Kalinin Chemical Works radioactive tracer methods have been used to develop a process for making synthetic corundum. Isotope techniques have been used to study flotation processes,[71] to investigate steam plants[72] and in other engineering fields.

The extent of the application of radioactive tracers in technology can be appreciated from the fact that at the All-Union Conference on the Use of Radioactive and Stable Isotopes in the National Economy and in Science (Technology) held in April 1957 over 180 papers were read.[73]

RADIOISOTOPES IN BIOLOGY AND MEDICINE

Artificial radioisotopes were first used in the U.S.S.R. in biology and medicine in 1939 in the departments of Biochemistry, and of Biophysics and Photobiology at the Gorky Institute of Experimental Medicine. These departments, assisted by the U.S.S.R. Academy of Sciences, Lebedev Physical Institute, set up measuring equipment, and made radioisotopes of phosphorus, and later on of bromine, by irradiating with radon and radium–beryllium sources. The results of the first investigations using phosphorus and bromine as radioactive indicators were reported at the Academy of Sciences Conference on the Physics of the Atomic Nucleus in 1940.[74–76]

The study of phosphorus metabolism[77] was the first application of radioactive isotopes to biology published in the U.S.S.R. At the same time, the Gorky Institute carried out an investigation of the assimilation rate of P^{32} into different organs of a tubercular patient,[78] and the disturbance of phosphorus exchange in the tuberculosis-damaged bones was examined.[79] It was found that mineral deficiency of injured bones is caused by an increased rate of exchange in the injured bone. Contemporary investigations in Leningrad dealt with phosphorus exchange in the central nervous system and the renewal of phosphorus-containing materials in human erythrocytes. This work was interrupted by the Second World War, and the results were not published until after the war.[80,81] During the same period E. N. Karger, who died during the war, started experiments on iodine exchange at the Timiryazev Biological Institute.

The first radioisotope laboratory in the U.S.S.R. for medical and biological research was set up by the Gorky Institute in 1940. In the same year, the Ukrainian Institute of Technical Physics was asked to begin the design of a linear accelerator, for the production of deuterons for medical and biological research.

The Second World War interrupted this work. This preparatory period played an important part in the subsequent rapid developments; it built up a nucleus of research workers who were experienced in the necessary experimental techniques and aware of the exceptional possibilities of tracer techniques for a wide variety of biological and medical problems. Immediately after the war, radioisotope work was resumed at an ever-increasing tempo, bringing within its scope an ever widening range of problems and attracting a variety of workers from scientific and medical centres, even before radioisotopes had been produced on an industrial scale.

One of the first postwar investigations was carried out at the Gorky University and the Gorky Medical Institute. P^{32} was used to study the effect of camphor and tetramethylammonium iodide on the rate of phosphorus exchange in organs and tissues of rats and frogs.[82] During this period research was started on a number of biological processes. Amongst these were the investigations of material exchange in the central nervous sytem, and the extension of researches in the physiology and biochemistry of digestion which had been interrupted during the war. This included research into phosphorus exchange, in particular in mice, into albumin exchange, and into bromine and iodine exchange. Work was carried out on the synthesis of amino-acids and the study of de-amination processes. Investigations of ion exchange were started, as also were the development of principles diagnosing mal-functioning of the thyroid gland using I^{131}, and the use of isotopes in microbiology. The first steps were made in the therapeutic use of isotopes. This work was reported at the All-Union Conference on the application of isotopes to biology and medicine.[83]

At present tracer methods are employed in almost all fields of biology and medicine. In keeping with the traditions of Soviet biological science, considerable attention has been paid to the study of the functions of

FIG. 2.

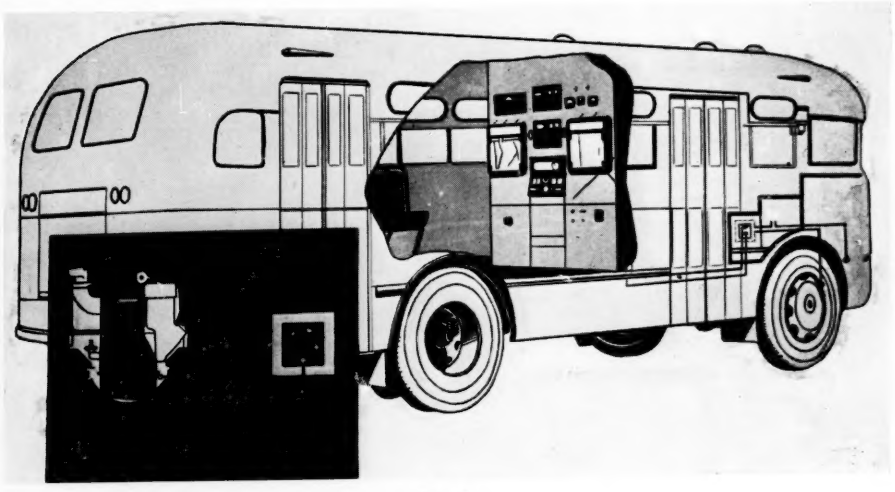

FIG. 3.

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the central nervous system. The most important achievements in this field are the results relating variations in metabolic rates to the functional state of the central nervous system. It has been demonstrated that phosphorus and albumin metabolism are accelerated by neural stimulus, and retarded by narcotic hypnosis and under hypothermic conditions. A detailed study of albumin metabolism in the cerebrum has provided information on the cytoarchitecture of the cerebral cortex.(84) The "conversion time" for phosphorus in adenosine triphosphate for different types of animals has been deduced from experiment.(85) Studies over several years have thrown fresh light on the absorption of the so-called "blood brain barrier", which is of importance in relation to conversion of phospholipides, and in particular the special part played by the phosphorus ethers of choline has been investigated. Br^{82} has been used to study the role of bromine in the functioning of the nervous system.(85)

To summarize, the use of radioactive isotopes has established a new field, which may be called functional biochemistry of the nervous system, since only by these techniques is it possible to observe the true rates of exchange processes, and to obtain a complete understanding of their qualitative aspects. Completely new data have been obtained from alimentary canal studies, particularly in the case of the formation and adsorption of bile.(86)

A series of investigations has been carried out with labelled micro-organisms, to study problems of pathogenesis and immunity against infections—in particular, dysentery. Important results have been obtained about the propagation in the organism of microbe cells and of labelled antigens of the dysentery bacteria. In particular the dependence of the absorption antigens on the method of application has been studied. These researches have initiated a new field of radio bacteriology and immunochemistry.(83) An exceptionally interesting and important application is the use of powerful γ-radiation sources in the manufacture of bacteriological preparations. Bacterial media have been sterilized, and paratyphoid and diphtheria vaccines have been prepared using radiation for their inactivation.(85)

Radioisotopes have been used in a large number of studies on the breeding of fish and farm animals.(85) For example, the use of Ca^{45} to study calcium exchange in laying hens showed a very high metabolic activity of calcium in the skeleton; S^{35} has been used to study the synthesis of keratin in wool, and radioisotopes have helped in the development and detailed study of the part played by the chlorophyll of growing fodder crops in haemoglobin synthesis in ruminants.

The application of isotopes in medicine has progressed in two directions: in the development of diagnostic techniques and in radiotherapy.

In the diagnostic application of I^{131} to the determination of the functioning of the thyroid gland, original methods of using radio-iodine have been developed to analyse the pathogenesis of its diseases; in particular, a relationship between the behaviour of I^{131} in the organism and the blood circulation(85) has been established. The study of this interrelation for different cardio-vascular diseases provided not only a firm basis for the differential diagnosis of thyroid disfunction, but has also led to the development of valuable diagnostic methods for the investigation of blood circulation. An original diagnostic use of radio-iodine has been developed in which the absorption of the thyroid gland is considered not only in relation to the activity of this organ, but in relation to the functioning of the organism as a whole.

A highly developed diagnostic use of radioisotopes is in blood circulation studies; techniques that have been developed include measurement of the velocity of the blood stream using Na^{23}, and determination of the circulating blood volume using appropriately labelled erythrocytes. A method for studying the resorption of sodium from subdermal deposits in various internal diseases should also be mentioned.

The effect of γ-radiation on the permeability of the haemato-encephalic and blood brain barriers for phosphorus–sodium

salts has been studied.[85] A detailed study has also been made of the state of the blood barriers in the clinical treatment of nervous diseases, in particular in lockjaw trauma and brain tumours.[85]

Several alternative methods have been suggested for studying the rapid movements of γ-emitting materials in the organism, in particular for the study of blood circulation.[87]

Successful methods have also been developed for the use of radioactive isotopes for diagnosis of cancer. In particular, work has been carried out on the location of surface tumours, metastases, and cancer of the womb by the selective absorption of P^{32} in the cancer tissue; valuable results have been obtained by examining radiation from the skin after introducing P^{32} in the localized area of the tumour in cancer of the mammary gland. A similar type of investigation has been conducted on the accumulation in tumours of isotopes introduced in anti-tumour serum.

The use of radioisotopes for therapy can be divided into three main categories. The first method, by external application of β-emitting materials, is employed extensively in various skin diseases; in cases of capillary angioma it is almost the only treatment giving effective results. The number of patients being given this treatment is of the order of several thousand.

The second method is to introduce therapeutic doses of artificially radioactive materials into the organism. One very widely applied technique is the use of radio-iodine in the treatment of thyrotoxicosis. So far there have been more than 2500 successful treatments of this disease in various hospitals in the U.S.S.R. Also in this category are many hundreds of cases of treatment of diseases of the blood-forming organs, such as erythraemia and leukaemia. In erythraemia the use of P^{32} introduced internally, gives prolonged and lasting results; in the case of leukaemia (in combination with other accepted methods), it is possible to arrest the progress of the disease, and in the case of a slowly developing process, make the patient fit to resume his daily work.

The third approach—external γ-radiation—is used both for superficial tumours and in the treatment of cancer of internal organs. Soviet γ-emitting machines loaded with Co^{60} have made possible an extensive network of Centres using this powerful remedy in the fight against these diseases. Both scientific research and clinical data show that, because of the strongly monochromatic nature of the radiation, side effects due to action on the skin are much less marked. In addition, since the machine can be loaded with a large amount of radioactive material equivalent to about 400 g radium, a very high radiation flux can be used, and the irradiation performed at much greater distances than would be possible using natural radium. This provides more favourable conditions for the distribution of deep-penetrating doses. At the same time, very extensive use is made of fine cobalt needles introduced into the tumorous tissue, and also of γ-emitting cobalt applicators for irradiation of superficial tumours. Results have also been obtained by introducing colloidal solutions of Au^{198}, in particular into the intraperitoneal region.[88,89]

The therapeutic application of radioactive isotopes developed on such a scale that in 1954 a conference was organized in the U.S.S.R. to discuss the use of P^{32} for the treatment of diseases of the blood-forming organs and for clinical investigations. The results of work on the use of Co^{60} were presented separately.

This work is carried out on a large scale throughout the Soviet Union, in particular at the Moscow and Leningrad Central Institutes.

RADIOISOTOPES IN AGRICULTURE

Radioisotopes are also widely used to study the mechanisms of processes taking place in plants. In plant physiology Bayer's theory, according to which the primary product of photosynthesis was formaldehyde formed by the hydration of carbon, was

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accepted for many years. It was assumed that in photosynthesis oxygen is obtained from carbon dioxide gas absorbed from the air. These concepts were refuted by the work of VINOGRADOV;[90] by using heavy oxygen he showed that in photosynthesis oxygen is obtained from water. A number of papers by foreign investigators, whose results have been confirmed in the U.S.S.R., showed that formaldehyde is not the primary product of photosynthesis, but the process is extremely complex, in that esters of phosphoric acid are formed. The chemical composition of the products of photosynthesis depends on a number of factors, including the spectral composition of the light causing it.[91] In addition to carbohydrates, albumins and other compounds are formed. Detailed schemes of photosynthesis are currently being studied. The theory that plants are fed by carbon dioxide from the atmospheric air was also modified and amplified following work by Kursanov, who used C^{14} to show that in photosynthesis plants also employ carbon dioxide entering the stem from the root system.[92] Radioactive isotopes were used to develop methods of feeding plants other than by their roots. This and other work revealed a close correlation between root feeding of plants and photosynthetic processes.

During a study of the biosynthetic function of chlorophyll the unexpected fact of the rapid renewal of chlorophyll in plant leaves[93] was discovered.

The study of the mechanisms of the rubber formations in plants showed that in koksaghyz (*Taraxacum koksaghyz*), rubber can be formed from carbohydrates.[94] It was shown that C^{14} atoms from labelled sugars, acetic and laevulinic acids, glycine and aceto-acetic acids are biosynthesized into rubber in almost the same manner but to a much lesser extent than from alanine-2 containing C^{14}.[95]

Much work has been devoted to the study of the effect of radiation on plant physiology. A recent paper of fundamental importance by VINOGRADOV shows that the presence of natural K^{40} has no effect on material exchange in the fungus *Aspergillus*.[96]

Using the radioisotope method, the existence of a material exchange between the graft and the sapling, and an interconnexion between the root system and the tops of trees, has been established. Fertilizers labelled with radioisotopes have been used to compare methods of adding fertilizers to soil; it has been shown that initially phosphorus is most efficiently absorbed from small grains, but during the later stages of plant growth it is absorbed more effectively from large grains. From this work, the optimum proportions of the components in mixed fertilizer have been deduced.[97] Marked improvement in the technique of using labelled atoms for the investigation of fertilizer absorption by plants was achieved by a new method based on "selective absorption". This method consists of introducing into the plant a standard labelled fertilizer and the unlabelled fertilizer to be investigated. By measuring the specific activity of the labelled element entering the plant, the relative absorption of the fertilizer under investigation can be calculated.[98]

The use of radioisotopes is employed on an ever-increasing scale by Soviet scientists in scientific research, industry, agriculture and medicine. The expansion of these investigations is illustrated by the increasing number of papers by Soviet authors, given at conferences on the applications of radioisotopes which are held both in the U.S.S.R. and abroad.

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Soviet Radiochemistry*

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THE study of radioactive substances began in the U.S.S.R. shortly after the discovery of the phenomenon of radioactivity by BECQUEREL in 1896.

At the beginning of the twentieth century A. P. SOKOLOV of Moscow University and I. I. BORGMAN of St. Petersburg University were studying the radioactivity of natural substances—medical earths, waters, rocks and the atmosphere. SOKOLOV introduced several improvements in methods of measuring radioactivity, developing in part, the well-known method of determining amounts of radium from the liberated radon. Other pre-revolutionary Russian scientists worthy of note are YU. N. ANTONOV, known for the discovery of uranium-Y in 1912, and L. S. KOLOVRAT-CHERVINSKY, who studied the emanating power of solid and fused salts.

However, the work of a few Russian scientists, often carried out abroad, does not permit us to speak of the existence of radiochemistry as a science in pre-revolutionary Russia. One of the reasons for the slow growth of radiological studies was the lack of radium and other radioactive elements. This lack was clearly recognized by the Russian scientist V. I. VERNADSKY, who organized a study of Russia's radioactive minerals, and in 1909 the Radium Commission of the Academy of Sciences was set up. However, attempts to organize the study of radioactive materials on a wider scale met with little encouragement until April 1918 when the Radium Commission of the Academy of Sciences decided to establish a factory for the extraction of radium from native minerals, and in spite of the difficulties arising from post-war disorder and civil war, V. G. KHLOPIN succeeded in 1921 in obtaining highly active radium preparations for the first time in our country. In 1922 V. I. VERNADSKY and V. G. KHLOPIN founded the Radium Institute of the Academy of Sciences of the U.S.S.R., thus confirming the emergence of Soviet radiochemistry.

RADIOELEMENTS IN PHYSICO-CHEMICAL SYSTEMS

Initially the work of V. G. KHLOPIN and his co-workers was concerned with the development of a method for the fractional precipitation of radium–barium salts and, in 1924, KHLOPIN established that the distribution of radium between crystals and mother liquor was in accordance with the law of BERTHELOT and NERNST. Also he showed that the law proved applicable to systems in which the "guest" component, a radium halide, being strongly diluted, was isomorphous with crystals of the "host", a barium halide. Later KHLOPIN and his pupil, B. A. NIKITIN, put forward the view that the applicability of the BERTHELOT–NERNST–KHLOPIN law to the distribution of any micro-component in the systems solution–precipitate and precipitate–gas was evidence of complete isomorphism between corresponding compounds of the "guest" and the "host". According to the relationship obtained by A. P. RATNER, the partition coefficient for the micro-component is determined by the difference in the chemical potentials of the ion under investigation in pure crystals and in mixed crystals, and by

* Translated by J. M. CRABTREE from *Atomnaya Energiya* **3**, No. 11, 459 (1957).

the activities of saturated solutions of the macro- and micro-components above the pure crystals. Recent studies carried out in the Soviet Union[1] and abroad have shown that Ratner's relationship is very useful in the study of the thermodynamics of isomorphous mixed crystals.

V. G. KHLOPIN and his co-workers, A. E. POLESITSKY, A. P. RATNER and P. I. TOLMACHEV, have studied the mechanism of equilibration of concentration of the micro-component in the crystalline phase and have shown that equilibration takes place by way of recrystallization of the solid salt. Study of the process of distribution of radium between a solution and crystals of appropriate isomorphous salts has shown that the distribution is also based on recrystallization of the precipitate.

Investigations of co-precipitation, using synthetic radioactive elements including neptunium, plutonium and americium as well as naturally radioactive ones, have been carried out in the Radium Institute of the Academy of Sciences of the U.S.S.R.[3] Such investigations have substantially broadened our ideas about the mechanism of the formation of mixed crystals of various types. For GRIMM's crystals and anomalous mixed ones, concentration limits were found,[4] below which mixed crystals were not formed. As well as the anomalous mixed crystals having a low limit, systems have been found,[5] having Pu^{4+} and Np^{4+} as micro-components and $K_3La(SO_4)_3$,K_2SO_4 as macro-components, whose coefficient of crystallization remains constant even at concentrations of the order 10^{-9} M.[5]

Extraction and sorption methods for the isolation of radioelements have been developed by Soviet radiochemists in connexion with the peaceful uses of nuclear energy. From detailed study of the extraction by organic solvents of radioactive isotopes from aqueous solutions,[6] several general conclusions have been drawn which relate the extracting power of the organic solvents to their structure. Spectrophotometric methods have been widely used to determine the state of a range of radioactive elements in non-aqueous solutions. Recently, extraction methods have been extended to the trans-plutonic elements.

The adsorption of radioelements on crystalline precipitates, glass, charcoal, silica leg and other materials has been studied.[7] Study of the adsorption of polonium by various agents[8] first showed the existence of colloidally dissolved radioelements. The formation of radiocolloids has been studied further, using various experimental methods including electrochemistry, ultrafiltration, centrifuging, and radiography.[9]

Researches into ion-exchange and chromatographic separation methods for radioelements have been carried out in many laboratories of the Soviet Union. The separation of uranium and thorium, for a wide range of thorium concentrations, has also been investigated and a chromatographic method for the purification of various solutions contaminated with micro-quantities of zirconium and niobium has been developed.[10] The selective adsorption of radioelements on various adsorption agents, including ion-exchange resins, silica gel, activated charcoal in hydrogen and oxygen atmospheres, has been studied.[11]

A method has been developed[12] for studying processes of complex formation in solution. The method is based on the simultaneous absorption of the central ion on anion and cation resins, and has been used to study the state of micro-quantities of fission product elements, including zirconium, niobium, and yttrium, in mineral and organic acid solutions. Also, methods of separating chromatographically the rare earth and transuranic elements have been substantially improved.[13]

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CHEMISTRY OF THE RADIOELEMENTS

Study of the distribution of radon in the systems Rn—H_2S, $6H_2O$; Rn—SO_2, $6H_2O$; Rn—H_2S, $3C_6H_5OH$; Rn—H_2S, $2C_6H_5CH_3$; Rn—H_2S, $3ClC_6H_4OH$, and others has led to a method of obtaining several compounds of the inert gases by isomorphous

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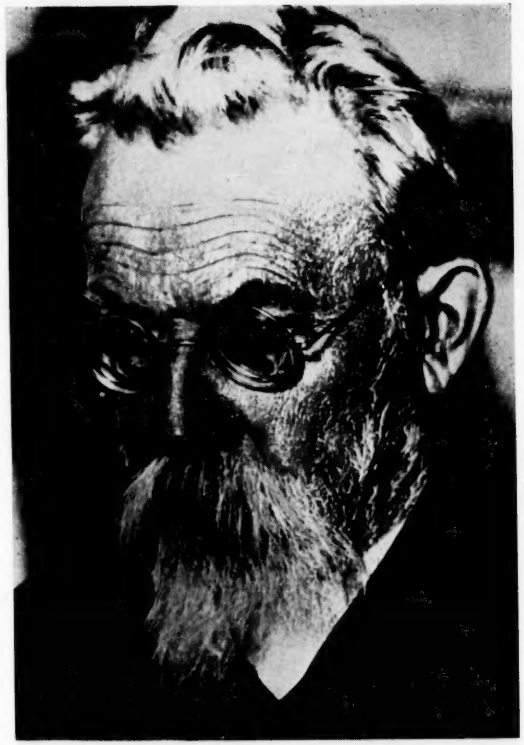
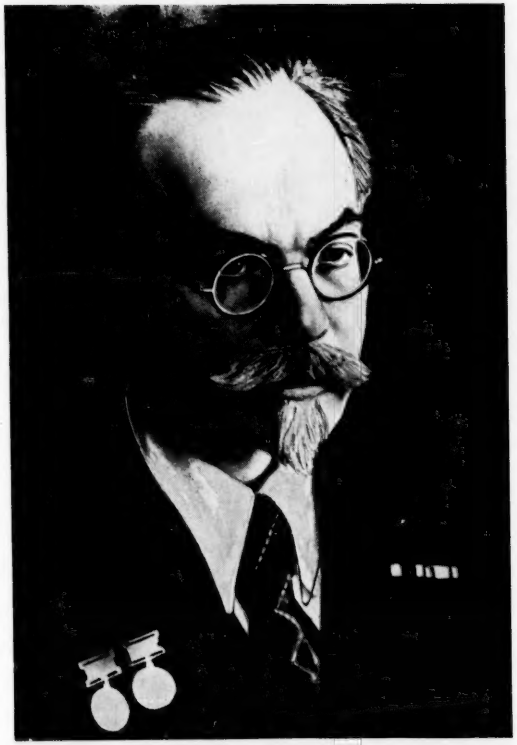


V. I. Vernadsky



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co-precipitation, and of establishing their composition.[14] Quantitative chemical separation of radon from helium, neon from argon, and argon from helium and neon has been carried out by making use of the different stabilities of the hydrates of the individual inert gases.

Until recently, weighable amounts of polonium have not been available to investigators and its chemical properties have been studied in tracer quantities only, usually by the method of isomorphous co-crystallization. Using the same method,[15] compounds of polonium having valencies of -2 and $+6$ have been identified for the first time. Also, organic compounds of bivalent polonium $(CH_3)_2PoI_2$ have been synthesized.[16]

Electrochemical studies of polonium were begun in 1946,[17] when a method of determining the electrode potentials of radioelements was proposed and developed. The method was a modification of the method of HEVESY and PANETH and has led to a more precise knowledge of the secretion of polonium in gold and platinum. The valencies of polonium in the normal and reduced states have been found to be $+4$ and $+2$, respectively, and the form of polonium ions in several compounds has been studied. The disproportionality of tetravalent polonium has also been established and the electrode potentials for hexavalent polonium studied.

An entirely different picture from that of polonium is presented by the chemistry of uranium and thorium. These elements are available in weighable quantities in almost any chemical laboratory and therefore available for analysis by classical methods. The number of completed investigations in the field is extremely large and reference will be made here to only a few.

Various methods of analysing uranium have been developed, including spectroscopy, X-ray spectroscopy, polarography, and luminescence. Special attention has been paid to direct physico-chemical methods of determining the amounts of impurities in uranium without previous chemical separation.[18]

Important work has been done on the inorganic chemistry of uranium and thorium. A series of complex acid salts of the type $H_4U(C_2O_4)_4$ has been made and their physico-chemical properties studied. It has been shown that the hexahydrated oxalate of uranium has substantially stronger acidic properties than the corresponding compound of thorium. A method has been developed for reducing U(VI) with rongalite.[19] The conditions have been determined for the existence of a series of peroxide compounds of uranium that are formed in the system $UO_2(NO_3)_2$—NaOH—H_2O_2—H_2O. The simplest formulae for the series have been given as $H_2U_2O_9$, $HU_2O_9^-$; $U_2O_9^{-2}$; UO_6^{-2}; UO_6^{-2}; HUO_8^{-3}; UO_8^{-4}; $Na_2U_2O_9$, $6H_2O$ and $Na_8U_4O_{22}3H_2O$.[20] The chemistry of the oxides and several halides of uranium has been studied and investigations into the photochemistry of aqueous solutions of uranium and thorium have been completed.[12]

Out of the large amount of work which has been done on the chemistry of the other radioelements the following results are worthy of note. A new method has been developed for determining quickly, with zirconium mandelate, amounts of protoactinium. The method achieves complete separation of protoactinium from all natural α-active radioelements.[22] A study has been made of the valence states of technetium and has led to the development of separation methods for it.[23] A sulphate separation method for plutonium and neptunium has also been developed.[24]

Soviet investigators have developed methods for the recovery of neptunium and plutonium[25] and americium[26] from fission products while the chemical properties of plutonium, americium and curium have been studied.[27] In studying the chemistry of tracer quantities of these elements a co-precipitation method was used. The formation of complex ions of plutonium and americium in inorganic acids has been studied by spectrophotometric means while electromigration and electrochemical investigations have been carried out, the self-reduction of Am(VI) and disproportionality of Am(V) being observed.

Numerous examples of the use of radio-

activity in chemical studies are given in the article entitled "Radioisotopes in the U.S.S.R." (*ibid*). It is, therefore, necessary to mention here only the study of the SZILARD–CHALMERS effect in which changes in the chemical state of elements, during the nuclear reactions (n, γ) and (γ, n), and nuclear transmutations, were examined and led to the development of efficient methods of concentrating the radioactive isotopes of silicon, phosphorus, chromium, germanium, arsenic, molybdenum, indium, tin, sulphur, tungsten, rhenium, mercury, bismuth, and tellurium. Original methods for the separation of isomers and the synthesis of labelled molecules were also developed.[28]

CHEMICAL METHODS OF STUDYING NUCLEAR REACTIONS

Studies of the chemical nature of fission products were begun in the U.S.S.R. earlier than the discovery of atomic fission, and soon after FERMI's first experiments in which neutrons were used to produce artificial radioelements, the inert gases xenon and krypton[29] were found in fission products. Later, the products of the fission of thorium by neutrons were studied.[30] The gaseous products of spontaneous fission of uranium nuclei were found in uranium minerals in 1947.[31]

In recent years, the products of fission have been studied by a wide range of chemical methods. Together with the fission products arising from the exposure of atomic nuclei to neutrons, those arising from exposure of nuclei to γ-quanta[32] and heavy ions have been studied. Radiochemical studies of fission products contained in the atmosphere, rainfall, natural waters and soils have great theoretical and practical importance, and the systematic studies that have been made show a gradual accumulation of long-lived radioactive nuclides in the atmosphere, soil and exposed reservoirs.

Mass-spectrometric methods for determining the yields of reaction products from the separation of uranium and plutonium isotopes have been developed, and have considerably speeded up and increased the accuracy of analysis.[33]

A radiochemical study of the interaction of protons, of energies up to 680 MeV, with complex nuclei was begun immediately the large synchrocyclotron of the United Institute for Nuclear Research became available. The study has embraced atomic nuclei of a wide range of atomic number and mass number, including aluminium, copper, silver, lanthanum, tantalum, tungsten, bismuth, thorium and uranium and qualitative and quantitative regularities occurring in the process of fission have been explained.[34] Fission of the silver nucleus has been observed and the influence of the shell structure of the product nuclei on yield, has been shown. The distribution of nuclei, formed in meteorites under the action of cosmic radiation, has been shown to be regular. Many previously unknown radioactive isotopes, mainly neutron deficient, have been detected and identified, and their spectra have been intensively studied by the methods of magnetic and scintillation γ-spectroscopy.[35] The decay schemes and energy levels for a series of nuclides have been established and fit in well with modern theories of the structure of complex nuclei.

In a short survey it is impossible to mention all the scientific trends being vigorously developed in the U.S.S.R. The growth in scientific production by Soviet scientists over the past two or three years and the close links of our native radiochemistry with industry, medicine, biology and agriculture give rise to the hope that the further development of nuclear science and its peaceful applications will be promoted.

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Cyclotron-produced Carrier-free Radioisotopes

Thick Target Yield Data and Carrier-free Separation Procedures

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A program has been undertaken for the production, processing and distribution of cyclotron-produced, carrier-free radioisotopes on a world-wide basis. Although cyclotron-produced radioisotopes are inherently more expensive than reactor-produced radioisotopes, several conditions are enumerated under which their use is desirable, and in many cases mandatory. Several new isotopes, previously considered difficult to obtain, are now readily available. Procedures are detailed for the separation of 17 radioisotopes in carrier-free form: Be^{7}, Na^{22}, V^{48}, Mn^{52}, Mn^{54}, Fe^{55}, Co^{57}, Zn^{65}, Ga^{67}, As^{74}, Sr^{85}, Y^{88}, Cd^{109}, In^{111}, Ce^{139}, W^{181} and Bi^{207}. Thick target yields are given for production of these radioisotopes from cyclotron irradiations with deuterons of 15 MeV energy and with protons of 8, 15 and 20 MeV energies.

RADIOISOTOPES SANS ENTRAINEUR PRODUITS DU CYCLOTRON

Un programme a été entrepris pour produire, préparer et distribuer à l'échelle mondiale les radioisotopes sans entraîneurs, produits au moyen du cyclotron. Quoique les radioisotopes venant du cyclotron sont en euxmême plus coûteux que ceux produits dans un réacteur, plusieurs conditions sont énumérées où leur emploi est préférable et en bien des cas obligatoire. Plusieurs nouveaux isotopes, autrefois considérés comme difficiles à obtenir, sont maintenant facilement disponibles. On détaille des procédés pour la séparation de 17 radioisotopes dans l'état sans entraîneur: Be^{7}, Na^{22}, V^{48}, Mn^{52}, Mn^{54}, Fe^{55}, Co^{57}, Zn^{65}, Ga^{67}, As^{74}, Sr^{85}, Y^{88}, Cd^{109}, In^{111}, Ce^{139}, W^{181} and Bi^{207}. Les rendements pour targes épaisses sont donnés pour la production de ces radioisotopes par des irradiations au cyclotron avec des deuterons d'une énergie de 15 MeV et avec des protons d'énergies de 8, 15 et 20 MeV.

TRÄGERFREIE RADIOISOTOPE AUS DEM ZYKLOTRON

Ein Programm auf weltweiter Basis zur Herstellung, Verarbeitung und Verteilung von trägerfreien Radioisotopen aus dem Zyklotron wurde aufgestellt. Obwohl die im Zyklotron hergestellten Radioisotope naturgemäss teurer sind als die im Reaktor hergestellten Isotope, besteht eine Reihe von Gründen, die ihre Verwendung wünschenswert erscheinen lassen und

in manchen Fälle sogar unbedingt erfordern. Mehrere neue Isotope, deren Herstellung ursprünglich schwierig erschien, sind nun erhältlich. Verfahren zur Abtrennung von 17 trägerfreien Radioisotopen werden in allen Einzelheiten angegeben: Be^{7}, Na^{22}, V^{48}, Mn^{52}, Mn^{54}, Fe^{55}, Co^{57}, Zn^{67}, As^{74}, Ca^{67}, Sr^{85}, Y^{88}, Ca^{109}, In^{111}, Ce^{139}, W^{181} and Bi^{207}. Ausbeuten aus dicken Targets für Zyklotronbestrahlung mit 15 MeV Deuteronen und 8, 15 und 20 MeV Protonen werden angegeben.

In October, 1955, a program was undertaken, with the approval of the United States Atomic Energy Commission,[1] to develop a commercial service for the production, processing and distribution of cyclotron-produced carrier-free radioisotopes on a world-wide basis. In the 3 years that this program has been in operation, it has been noted that the use of cyclotron-produced radioisotopes has steadily increased, although not as rapidly as the increase in the use of reactor-produced radioisotopes as announced by the USAEC.[2] The slower rate of increase can be attributed, in part, to the inherently greater expense in producing relatively small quantities of radioactivity in large and costly charged-particle accelerators. However, cyclotron-produced carrier-free radioisotopes do possess several properties which make their use desirable and in many cases mandatory.

A carrier-free isotope is characterized by having no measurable amounts of stable isotopes of the same element present. Carrier-free isotopes are produced by charged-particle irradiations, in which the atomic number (or the chemical identity) of the resulting radioactive atoms is changed from the atomic number of the original target material. With the use of special chemical separation techniques, such as ion exchange chromatography or solvent extraction, the minute amount of radioactive material can be separated from the macro quantity of target material, purified, and prepared as a carrier-free radioisotope. Carrier-free radioisotopes may be used in many ways. They may be injected into animals and humans where the chemical tolerance is low, e.g. As^{74}. They may be used for radiochemical studies at extremely low concentrations, ($<10^{-8}$ molar). They may be used for the preparation of weightless counting standards, eliminating corrections for self-absorption and scattering.

Charged-particle accelerators produce radioisotopes which are, in general, neutron deficient with respect to the nuclear stability line, and which decay by positron emission or electron capture. Reactor-produced radioisotopes, formed by neutron capture, are neutron excessive and decay by β-emission. The half-lives of radioisotopes of the same element are generally different. Thus, for many applications, a choice of radioisotopes of a given element, with different radiation characteristics, is available. For example, the shorter-lived 65-day Sr^{85}, adaptable to the convenient technique of scintillation counting, may be used in place of the toxic fission product ~30-year Sr^{90}, which decays by the emission of β-particles only. The longer-lived 2·6-year Na^{22} or 105-day Y^{88} may be used in applications where the half-lives of the isotopes 15-hour Na^{24} or 64-hour Y^{90} are too short. Cyclotron irradiation can often produce radioisotopes free of other radioactive isotopes of the same element, which otherwise can be obtained only by reactor irradiation of electromagnetically-enriched isotopes. For example, 3-year Fe^{55} can be prepared free of 45-day Fe^{59}. Finally, a number of elements do not possess usable radioisotopes which can be made by reactor irradiation. These include aluminum, titanium and vanadium. Cyclotron irradiations have been made for the production of ~10^{6}-year Al^{26}, 3·08-hour Ti^{45} and 16·2-day V^{48}.

The initiation of a program for the production and distribution of cyclotron-produced carrier-free radioisotopes required the development of a number of procedures which had not been previously reported, and

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the introductions of revisions into published procedures,[3,4] which were not entirely satisfactory for the intended use because of low chemical yield or an insufficient product purity.

Procedures have been reported for radiochemical separations of many of the elements for which artificially-produced radioactive isotopes exist.[5,6] However, these separations involve the addition of stable isotopes of the same element as carriers so that standard chemical operations can be performed with the submicrogram quantities of the radioactive species sought. Since carrier-free radioisotopes are the desired products, these separation techniques are generally unsuitable. Chemical separation procedures for the sub-microgram quantities of radioisotopes must be designed with techniques which are usually mass independent, such as co-precipitation with non-isotopic carriers, ion exchange chromatography and solvent extraction. The procedures, given in the appendix, were developed from these techniques.

Cyclotron yield data are found to be quite sparse. Some data have been reported,[7,8] and these were used as a guide in planning irradiations. Often, theoretical yield calculations are the only data available. Irradiations for the production of the carrier-free radioisotopes described in this paper were performed at the University of Pittsburgh cyclotron with protons of 8 MeV energy and deuterons of 15 MeV energy and at the Oak Ridge National Laboratory cyclotron with protons of 15 and 20 MeV energies.[7]

YIELD DATA

Table 1 lists the thick target yields of 17 radioisotopes obtained from irradiations performed during this program. Tabulated for each isotope are the target material, the incident particles used in the irradiation, the thick target yield corrected for losses incurred in chemical processing and decay from the time of the end of the irradiation to the time of assay, the thick target yield data in the literature for the same radioisotope and the major sources of uncertainties in the thick target yields determined in this program.

The thick target yield data were obtained by measurement of the duration and intensity of the irradiations, chemical processing of the irradiated targets, and radiometric assays of the isolated carrier-free activities. The integrated beam currents of the irradiations were given to the authors by the operating personnel of the respective cyclotrons. The yields of the activities following chemical isolation were determined by trial runs. Except for Fe^{55}, Cd^{109}, and W^{181}, assay of the isolated activity was made by γ-ray spectroscopy, using a well-type, thallium-activated sodium iodide scintillation counter equipped with a single channel pulse-height analyser. End window proportional flow counters were used for Fe^{55}, Cd^{109}, and W^{181}, which do not have prominent energetic γ-rays. Standard samples of several isotopes, obtained from either the National Bureau of Standards or through cross checking with other laboratories, were used to determine counter efficiencies for the various radiations of interest. Where standards for particular isotopes were not available, counter efficiencies were estimated by interpolation between available standards. For very low energy radiation, it was necessary to approximate efficiencies from the physical arrangement and the properties of the counter components. In general, assays could be made with less than 10 per cent absolute uncertainty.

Other major sources of uncertainty introduced into the thick target yield data originate from several sources. In most cases, the chemical yields were greater than 90 per cent and the probable errors assigned were of the order of 5 per cent or less. In a few cases, the chemical yield could not readily be determined and the probable error was as high as 30 per cent. In this group are included the short-lived isotopes, where need for total yield information is secondary to the need for rapid separation. Probable errors of the order of 5–10 per cent were assigned to the integrated current data. Target evaporation

TABLE 1. Thick target cyclotron yields

Isotope	Target	Incident particle	*Production rate mc/mA–hr* (this work)	(other work)		Major sources of uncertainty* (this work)
Be^{7}	Li	15 MeV deuterons	48 ± 10	low	(10)	a, e
		19 MeV deuterons		2 ± 25%	(9)	
		8 MeV protons	77 ± 12			a, e
		20 MeV protons	166 ± 25	170	(7)	c, f
Na^{22}	Mg	14 MeV deuterons		1 ± >25%	(9)	
		15 MeV deuterons	2·00 ± 0·15	1·75	(10)	e, f
		20 MeV protons		0·4	(7)	
V^{48}	Cr	15 MeV deuterons		low	(10)	
	Ti	15 MeV deuterons	75 ± 25			b, c
	TiO_2	15 MeV protons	125 ± 25			c
Mn^{52}	Cr	15 MeV deuterons	144 ± 20	3	(10)	b
		19 MeV deuterons		8 ± >25%	(9)	
		8 MeV protons	4·5 ± 2·0			a, b
		20 MeV protons		80	(7)	
Mn^{54}	Fe	14 MeV deuterons		0·10 ± >25%	(9)	
		15 MeV deuterons	1·4 ± 0·3			d, e
	Cr	20 MeV protons	0·5 ± 0·2	0·5	(7)	b
	80% Cr^{54}	20 MeV protons	87 ± 10			a
Fe^{55}	Mn	15 MeV deuterons	3·7 ± 0·7	0·67	(10)	a
		19 MeV deuterons		0·02 ± >25%	(9)	
		20 MeV protons	13·5 ± 5·0	10	(7)	
Co^{57}	Fe	15 MeV deuterons	9·5 ± 2·0			a, d
		19 MeV deuterons		5·0 ± >25%	(9)	
	Ni	20 MeV protons	22 ± 6	50	(7)	a
Zn^{65}	Cu	14 MeV deuterons		0·5 ± >25%	(9)	
		15 MeV deuterons		3·5	(10)	
		20 MeV protons	15 ± 1·5	9·3	(7)	a
Ga^{67}	Zn	15 MeV deuterons	58 ± 20			a, c
As^{74}	Ge	15 MeV deuterons	31 ± 10			a, b, c
		19 MeV deuterons		10 ± 25%	(9)	
		15 MeV protons	170 ± 50	50	(7)	a, b, c
Sr^{85}	RbCl	15 MeV deuterons	16 ± 6	0·13 ± 25%	(9)	e, f
		19 MeV deuterons		0·60 ± 25%	(9)	
		15 MeV protons	23 ± 4			e
Y^{88}	SrO	14 MeV deuterons		0·10 ± 25%	(9)	
		15 MeV deuterons		38	(10)	
		19 MeV deuterons		1·0 ± 25%	(9)	
		15 MeV protons	32 ± 3	20	(7)	a, e
Cd^{109}	Ag	15 MeV deuterons	2·6 ± 1·0			a, b
		19 MeV deuterons		2 ± >25%	(9)	
In^{111}	Cd	15 MeV deuterons	18 ± 12			a, c, d
Ce^{139}	La_2O_3	15 MeV deuterons	3·1 ± 1·6			a, c
		15 MeV protons	5·7 ± 2·9			a, c
W^{181}	Ta	15 MeV deuterons	4·5 ± 2			a, b, c
		19 MeV deuterons		0·0005 ± >25%	(9)	
Bi^{207}	Pb	20 MeV protons	0·8 ± 0·5			a, d, f

* Major sources of uncertainty:
a – small number of irradiations made.
b – chemical yield in doubt.
c – radiometric assay in doubt.
d – other radioisotopes interfered in radiometric assay.
e – beam current uncertain.
f – possible target evaporation.

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is considered as a potential source of non-reproducibility of yield from cyclotron irradiations where irradiations are made under unsealed conditions. This was particularly evident in irradiations performed with RbCl where larger than expected variations were found in Sr^{85} yield.

For some of the radioisotopes listed, other radioisotopes of the same element are produced. In these cases, since isolation of the desired isotope could not be achieved by chemical means, the assays proved to be more difficult. For example, two other radioactive isotopes of bismuth interfere with the radiometric assay of Bi^{207}. Mn^{54} requires an extensive delay period to allow the 6-day Mn^{52} isotope to decay sufficiently for an accurate assay of Mn^{54}. In addition, uncertainties in decay schemes and half-lives introduce some errors in the yield determinations.

CHEMICAL PROCEDURES

The chemical separation procedures given in the appendix have been used successfully by the authors, many of them on a routine basis. The procedures have been necessarily developed with techniques normally employed for carrier-free separations. Every procedure utilizes the techniques of co-precipitation with non-isotopic carrier, ion exchange chromatography, or solvent extraction, or combinations of these. It has been found that many of the reagent volumes and concentrations are critical, and large deviations from the stated conditions often result in poor yields or in incomplete decontamination.

Although the product isotopes obtained are nominally carrier-free, i.e. no non-active atoms have been added intentionally, some non-active material is invariably present. The sources of this contamination are impurities in the target material and in the reagents used in the separation. In principle, virtually carrier-free products could be obtained by careful purification of the target material and the reagents used.

All chemistry operations are performed in Pyrex glassware except for Na^{22} and for procedures in which HF is used. To minimize exchange of Na^{22} with the sodium present in the glass, Vycor utensils are used. Polyethylene or other HF-inert materials are used to contain HF solutions.

APPENDIX

Carrier-free Separation Procedures for Radioisotopes listed in this Paper

1. *Be^7.* Target Material: *lithium.*
Product: 99+% *Be^7, in HNO_3 or HCl solution.*
Production Reactions: *$Li^7(p,n)Be^7$ or $Li^7(d,2n)Be^7$*
Other Important Reactions: *None.*
Chemical Separation Principles: *Be^7 is carried on $Fe(OH)_3$. Fe^{III} is then removed by ion exchange.*
Source Reference: (11).
Recovery 98%. Time Required: ~4 *hr.*

The lithium metal, about 10 g, is etched from its copper backing with 0·02 N HCl. After acidification of the resulting solution with HCl, any solids present are removed by filtration. Thirty milligrams of Fe^{III} carrier are then added, and the solution is made just ammoniacal. After digesting for 1 hr, the $Fe(OH)_3$ is separated by filtration through no. 42 Whatman filter paper. The Be^7 activity is quantitatively retained by the precipitate.

The precipitate is dissolved in a minimum of HCl and then reprecipitated with NH_4OH. After digesting for 1 hr, the precipitate is separated by centrifugation and washed twice with water, then dissolved in 5 ml 12 N HCl.

An Amberlite IRA-400 column is prepared, and conditioned with 12 N HCl. The solution is passed through this column, the iron being retained and the Be^7 passing through. The column is washed with three column volumes of 12 N HCl.

The entire eluate is evaporated to near dryness and treated with HNO_3 to destroy organic matter. If desired, the Be^7 can be converted to the chloride by repeated evaporation with HCl.

2. *Na^{22}.* Target Material: *magnesium.*
Product: 99+% *Na^{22}, in HNO_3 or HCl solution.*
Production Reactions: *$Mg^{24}(d,\alpha)Na^{22}$.*
Other Important Reactions: *$Mg^{25}(d,n)Al^{26}$; $Mg^{26}(d,2n)Al^{26}$.*
Chemical Separation Principles: *Al^{26} is removed by*

carrying on $Be(OH)_2$. Most of the magnesium is removed by precipitation with NH_3. Residual magnesium is removed by ion exchange. Source Reference: (12)(13). Recovery: 96%. Time Required: ~12 *hr.*

The magnesium cup target is floated on 50 ml of water in a Vycor beaker. Small portions of HCl are added until the activity is entirely removed. About 10 g of magnesium are dissolved, 25 ml of HCl added, and the solution diluted to 200 ml. Solids are then removed by filtration.

In order to recover the Al^{26} in the solution, 25 mg of beryllium carrier are added and the solution brought to a methyl red endpoint with NH_4OH. After cooling to room temperature, the $Be(OH)_2$ is removed by centrifugation, washed twice with water, and reserved for Al^{26} recovery.

The supernatant solution is evaporated to 100 ml and saturated with NH_3 gas, in an ice bath. The $Mg(OH)_2$ precipitate is removed by filtration, with suction, through a fritted glass funnel. The precipitate is slurried in the funnel three times with NH_4OH and dried by suction each time.

The filtrate and washings are combined and evaporated to near dryness, 25 ml of HNO_3 added, and the solution is evaporated to near dryness. This operation is repeated twice to remove the NH_4Cl present. To the residue of the last evaporation, 25 ml of water is added. If insoluble material is present, it is removed by filtration.

A Dowex-50 column is conditioned with 2 N NH_4OH until the effluent reaches a pH of 9. The solution is passed through the column at a rate of about 0·3 ml/min/cm^2. The column is washed with 200 ml of water. The Na^{22} is then eluted with 0·35 N HCl.

The eluate is evaporated to near dryness in a Vycor beaker and NH_4Cl is again removed with HNO_3. Organic material is also removed by treatment with HNO_3. If desired, the Na^{22} can be prepared carrier-free, in HCl solution, by repeated evaporations with HCl.

In cases where inactive sodium is known to be present in the magnesium target, or where a specific activity of the order of 10 c/g is acceptable, the procedure may be shortened somewhat. If 1 mg of sodium is present, the gross decontamination step can be effected by precipitation of sodium magnesium uranyl acetate, as outlined by IRVINE *et al.*[12] Uranium is precipitated with NH_4OH and residual magnesium is then removed by cation exchange as outlined above.

Al^{26} can be recovered by a method outlined by RIGHTMIRE *et al.*[13]

3. V^{48}. Target Material: *titanium dioxide.* Product: 98+% V^{48} + V^{49} *in HNO_3 or HCl solution.*
Production Reactions: $Ti^{47}(d,n)V^{48}$; $Ti^{48}(d,2n)V^{48}$; $Ti^{48}(d,n)V^{49}$; $Ti^{49}(d,2n)V^{49}$.
Other Important Reactions: $Ti^{46}(d,\alpha)Sc^{44}$; $Ti^{48}(d,\alpha)Sc^{46}$; $Ti^{49}(d,\alpha)Sc^{47}$; $Ti^{46}(d,2p)Sc^{46}$; $Ti^{48}(d,\alpha p)Ca^{45}$; $Ti^{46}(d,n)V^{47}$; $Ti^{47}(d,2n)V^{47}$;
Chemical Separation Principles: *A Na_2CO_3–$NaNO_3$ fusion of the dissolved target results in insoluble TiO_2 and a soluble vanadate compound. Scandium and calcium are co-precipitated with $Fe(OH)_3$ from strong NaOH solution. Vanadium, as vanadyl ion, is carried on $Fe(OH)_3$ under controlled pH conditions. Iron is removed by ion exchange.* Source Reference: (14). Recovery: ~90%. Time Required: ~6 *hr.*

The target, about 5 g of titanium dioxide, is ground to a fine powder and placed in a nickel crucible. Ten grams of Na_2CO_3 and 0·2 g of $NaNO_3$ are added, and the solids are mixed thoroughly.

The mixture is fused at 700°C for 45 min. The melt is cooled, ground, and leached with cold water to dissolve the vanadium. The volume is reduced to 100 ml by evaporation, 10 mg of Fe^{III} carrier is added, an excess of NaOH is added to precipitate $Fe(OH)_3$. The precipitation is repeated and serves to scavenge calcium and scandium.

After removing the $Fe(OH)_3$ by centrifugation, the solution is acidified and heated to expel CO_2. Ten milligrams of Fe^{III} carrier are added and the pH is carefully adjusted to 6·2 with NH_4OH. After digesting for 30 min, the $Fe(OH)_3$ is separated by centrifugation. Vanadium, presumably as vanadyl ion, is retained quantitatively by the precipitate. The precipitation is repeated twice more, and the final precipitate is dissolved in a minimum of 4 N HCl. The solution is passed through an Amberlite IRA-400 column which has been conditioned with 4 N HCl. A 4 N HCl wash serves to remove the residual vanadium activity from the column. The eluate is evaporated to near dryness, and then treated with HNO_3 to remove NH_4Cl and to destroy organic matter. A chloride solution can be obtained by evaporation with HCl.

It should be noted that this procedure will not remove aluminum. The target backing or container should be nickel.

4. Mn^{52} *and* Mn^{54}. Target Material: *chromium.* Product: 98+% Mn^{52} + Mn^{54}, *in HNO_3 or HCl solution.*
Production Reactions: *A. deuteron bombardment* $Cr^{52}(d,2n)Mn^{52}$; $Cr^{53}(d,n)Mn^{54}$; $Cr^{54}(d,2n)Mn^{54}$. *B. proton bombardment* $Cr^{52}(p,n)Mn^{52}$; $Cr^{53}(p,2n)Mn^{52}$ $Cr^{54}(p,n)Mn^{54}$.
Other Important Reactions: *A. deuteron bombardment* $Cr^{50}(d,\alpha)V^{48}$. *B. proton bombardment* $Cr^{50}(p,2p)V^{49}$
Chemical Separation Principles: Mn^{52} *and* Mn^{54}

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are carried on $Fe(OH)_3$ from NaOH–Br_2 solution. Chromium and vanadium are retained in the supernatant liquid. Mn^{52} and Mn^{54} are carried on $Fe(OH)_3$ from NH_4OH to separate from residual sodium. Iron is removed by ion exchange. Source Reference: (15).
Recovery: ~95%. Time Required: ~6 *hr.*

The chromium is etched from its copper backing with HCl; 10–15 g are dissolved. Twenty milligrams of Fe^{III} are added, and the solution evaporated to near dryness. The residue is dissolved in a minimum of HCl, and the volume adjusted to 25 ml. The solution is poured, with stirring, into 300 ml of cold 7 N NaOH which has been saturated with liquid bromine. The resulting $Fe(OH)_3$ precipitate quantitatively carries manganese, while chromium and vanadium are retained in the supernate.

After digesting on a hot-plate for 30 min, the precipitate is separated by filtration through a fritted glass funnel, with suction. The precipitate is washed with water until no color can be detected in the wash water, then dissolved in a minimum of 1 N HCl. The precipitation (using 150 ml of the NaOH–Br_2 solution), filtration, and washing are then repeated three times. The last precipitate is dissolved in a minimum of HCl, and an excess of NH_4OH is added to precipitate $Fe(OH)_3$. This precipitation is repeated twice to separate the activity from residual sodium. The final precipitate is dissolved in 5 ml of 4 N HCl.

An Amberlite IRA-400 column is conditioned with 4 N HCl. The solution is passed through the column and the activity is washed through with 4 N HCl. Iron is retained by the column.

The eluate is evaporated to near dryness and treated with HNO_3 to remove organic matter. If desired, the Mn^{52} can be obtained in an HCl solution by repeated evaporation with HCl.

5. *Mn^{54} and Co^{56}, Co^{57}, Co^{58}.* Target Material: *iron.*
Product: 98+% *Mn^{54} and* 98+% *pure combined cobalt activity, in HNO_3, or HCl solution.*
Production Reactions: $Fe^{56}(d,\alpha)Mn^{54}$; $Fe^{56}(d,2n)Co^{56}$; $Fe^{56}(d,n)Co^{57}$; $Fe^{57}(d,2n)Co^{57}$; $Fe^{57}(d,n)Co^{58}$; $Fe^{58}(d,2n)Co^{58}$.
Other Important Reactions: $Fe^{54}(d,\alpha)Mn^{52}$.
Chemical Separation Principles: *Iron is extracted with ethyl ether. Manganese and cobalt are selectively eluted from an anion exchanger.*
Source Reference: (16).
Recovery: 98% Time Required: ~8 *hr.*

The iron target is etched with HCl until essentially all the activity is in solution. About 10 g are dissolved. Twenty milliliters of cold liquid bromine are added to oxidize the iron present to Fe^{III}. The solution is allowed to stand for 2 hr, and is then evaporated to 40 ml. Iron is extracted with ethyl ether, three extractions removing more than 95 per cent of the iron.

The solution is evaporated to near dryness and 5 ml of 8 N HCl are added. A Dowex-1 column is prepared, and conditioned with 8 N HCl. The solution is passed through the column, and the manganese is eluted with 8 N HCl. Ten milliliter fractions are collected and monitored for activity. When the manganese has been completely eluted, the eluant is changed to 4 N HCl to remove the cobalt. Ten milliliter fractions are collected and monitored. Iron remains on the column.

Both the cobalt and manganese fractions are treated with HNO_3 to remove organic matter. Either activity can be converted to the chloride by repeated evaporations with HCl.

6. *Fe^{55}.* Target Material: *manganese.*
Product: 99+% *Fe^{55}, in HNO_3 or HCl solution.*
Production Reactions: $Mn^{55}(p,n)Fe^{55}$; *or* $Mn^{55}(d,2n)Fe^{55}$.
Other Important Reactions: *none.*
Chemical Separation Principles: *Manganese is separated by ion exchange.* Source Reference: (17).
Recovery: 99%. Time Required: ~4 *hr.*

The manganese is etched from its backing with HCl. About 10 g are dissolved. The resulting solution is evaporated to 20 ml and diluted with water to 40 ml.

A Dowex-1 column is conditioned with 4 N HCl and the solution passed through the column. Iron is retained, and manganese is eluted from the column with 4 N HCl.

The Fe^{55} is then eluted with 0·5 N HCl. The eluate is evaporated to near dryness and treated with HNO_3 to remove organic matter. An HCl solution can be obtained by repeated HCl evaporation.

7. *Zn^{65}.* Target Material: *copper.*
Product: 99+% *Zn^{65}, in HNO_3 or HCl solution.*
Production Reactions: $Cu^{65}(d,2n)Zn^{65}$; *or* $Cu^{65}(p,n)Zn^{65}$.
Other Important Reactions: $Cu^{65}(d,\alpha)Ni^{63}$; $Cu^{63}(d,\alpha p)Co^{60}$.
Chemical Separation Principles: *Zn^{65} is retained by an anion exchanger in weak HCl while the other divalent transition elements are not.* Source Reference: (17).
Recovery: 98%. Time Required: ~5 *hr.*

The activity is etched from the copper target with 1 N HNO_3. Between 5 and 10 g are dissolved. The resulting solution is evaporated to dryness and converted to chloride by evaporation with HCl. After evaporating to dryness, the residue is dissolved in a minimum of 1 N HCl.

A Dowex-1 column is prepared and conditioned with 1 N HCl. The solution is passed through the column, which is then washed with 1 N HCl until copper cannot be dectected by H_2S addition in the effluent. Nickel and cobalt are not retained. Zinc is then eluted with 0·0005 N HCl.

The solution is evaporated to near dryness and treated with HNO_3 to remove organic matter. A chloride solution can be obtained by HCl evaporations.

8. Ga^{67}. Target Material: *zinc.*
Product: 98+% Ga^{67} *pure combined gallium activities in* HNO_3 *or HCl solution.*
Production Reactions: $Zn^{66}(d,n)Ga^{67}$; $Zn^{67}(d,2n)Ga^{67}$.
Other Important Reactions: $Zn^{66}(d,2n)Ga^{66}$; $Zn^{67}(d,n)Ga^{68}$; $Zn^{68}(d,2n)Ga^{68}$; $Zn^{66}(d,\alpha)Cu^{64}$.
Chemical Separation Principles: *Gallium is carried on* $Fe(OH)_3$ *from* NH_4OH *solution. Copper is retained in the supernate. Iron is removed by precipitation from strong KOH solution. Potassium and residual copper are separated by ion exchange.*
Recovery: 80+%. Time Required: ~6 *hr.*

The zinc target, about 5 g, is dissolved in a minimum of HCl. The solution is diluted to 100 ml. Twenty milligrams each of Fe^{III} and Cu^{II} carriers are added. The pH is carefully adjusted to 5·5 with NH_4OH, and the solution is allowed to digest for 15 min. The precipitate is removed by centrifugation and dissolved in HCl. A second precipitation is performed to insure separation from copper.

The last precipitate is dissolved in a minimum of HCl, the volume is adjusted to 20 ml with water, and an excess of KOH is added. After heating to a boil, the precipitate is separated by centrifugation and the supernate, containing the activity as gallate ion, is reserved. The precipitate is dissolved in HCl, and a second precipitation is performed. The supernates are combined, neutralized with HCl, and excess HCl is added to yield a solution 3 N in HCl.

The solution is passed through a Dowex-1 column which has been conditioned with 3 N HCl. Three column volumes of 3 N HCl are passed through the column to remove potassium and residual copper. Gallium is eluted with 0·2 N HCl.

After evaporating the solution to near dryness, organic matter is removed by evaporation with HNO_3. Conversion to chloride can be effected by evaporation with HCl.

9. As^{73}, As^{74}. Target Material: *germanium.*
Product: 98+% As^{73}+ As^{74}, *in HCl–*Cl_2 *solution.*
Production Reactions: $Ge^{72}(d,n)As^{73}$; $Ge^{73}(d,2n)As^{73}$; $Ge^{73}(d,n)As^{74}$; $Ge^{74}(d,2n)As^{74}$.
Other Important Reactions: $Ge^{70}(d,n)As^{71}(\beta)Ge^{71}$.
Chemical Separation Principles: *Germanium is removed by distillation from HCl in the presence of* Cl_2. *Arsenic is then distilled from an HCl–CuCl medium.*
Recovery: 90+%. Time Required: ~6 *hr.*

The germanium target, about 5 g, is aged for 10–15 days to allow the As^{71} to decay, and is then dissolved in aqua regia. The solution is evaporated to near dryness twice while passing chlorine gas through rapidly. After diluting with 15 ml HCl, the solution is transferred to a distilling flask which has a diptube so that a constant gas flow can be forced through the solution during distillation.

Germanium is distilled into a trap containing 6 N NaOH while passing chlorine gas through the still. The solution is evaporated to near dryness several times, with additions of HCl between evaporations. A total volume of 25–35 ml is distilled.

Arsenic is then distilled into an ice-cooled water trap by adding 5 ml of a saturated HCl solution of CuCl to the still and passing HCl gas through the still. Distillation is continued until activity cannot be detected in the distillate.

The active distillate is evaporated to the desired volume, while bubbling chlorine gas into the liquid.

10. Sr^{85}. Target Material: *RbCl.*
Product: 99+% Sr^{85}, *in* HNO_3 *or HCl solution.*
Production Reactions: $Rb^{85}(p,n)Sr^{85}$; *or* $Rb^{85}(d,2n)Sr^{85}$.
Other Important Reactions: $Rb^{87}(d,\alpha)Kr^{85}$.
Chemical Separation Principles: Sr^{85} *is carried on* $Pb(NO_3)_2$, Kr^{85} *volatilizes during sample dissolution. The lead carrier is then removed as PbS.*
Source Reference: (18).
Recovery: 98%. Time Required: 3 *hr.*

The RbCl, about 5 g, is dissolved in water, acidified, and filtered. Ten milligrams of lead carrier are added and the solution evaporated to 1 ml. Thirty milliliters of fuming HNO_3 are added and the solution cooled in an ice bath, with occasional stirring.

$Pb(NO_3)_2$, which carries the Sr^{85} quantitatively, is removed by centrifugation, dissolved in a minimum of water, and reprecipitated. The $Pb(NO_3)_2$ is separated by centrifugation, and dissolved in 25 ml of water.

PbS is precipitated by saturating the solution with H_2S. Sr^{85} is quantitatively retained in the supernate. The solution is filtered, evaporated to near dryness, and the activity dissolved in HCl or HNO_3.

11. Y^{88}. Target Material: *strontium oxide.*
Product: 98+% Y^{88}, *in* HNO_3 *or HCl.*
Production Reactions: $Sr^{88}(p,n)Y^{88}$.
Other Important Reactions: $Sr^{88}(p,2n)Y^{87}$.

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Chemical Separation Principles: *Y^{88} is carried on $Fe(OH)_3$. The Fe^{III} is removed by ion exchange.*
Recovery: 98%. Time Required: ~4 *hr.*

The SrO target, about 5 g, is dissolved in 0·1 N HCl. Ten milligrams of Fe^{III} carrier are added. Carbonate-free NH_4OH is added until the pH reaches 8·5. The $Fe(OH)_3$ precipitate, which carries Y^{88} quantitatively, is separated by centrifugation. Four reprecipitations are performed, using a minimum of HCl to dissolve the precipitates. The last precipitate is washed twice with water, then dissolved in a minimum of 6 N HCl.

The solution is passed through an Amberlite IRA-400 column which has been conditioned with 6 N HCl. The activity is washed from the column with 6 N HCl. The eluate is then evaporated to near dryness and treated with HNO_3 to destroy organic matter. The Y^{88} can then be converted to the chloride by evaporation with HCl.

It should be noted that if aluminum is present (from backing or container), several $Fe(OH)_3$ precipitations from strong NaOH should be performed.

12. *Cd^{109}.* Target Material: *silver.*
Product: 98+% *Cd^{109}, in HNO_3 or HCl solution.*
Production Reactions: *$Ag^{109}(p,n)Cd^{109}$ or $Ag^{109}(d,2n)Cd^{109}$.*
Other Important Reactions: *$Ag^{107}(p,n)Cd^{107}$ or $Ag^{107}(d,2n)Cd^{107}$; $Ag^{109}(d,\alpha)Pd^{107}$.*
Chemical Separation Principles: *Cd^{109} is extracted from a thiocyanate medium into chloroform–pyridine, back-extracted into 1 M HNO_3, and this cycle repeated. Final purification is effected by means of anion exchange.*
Source Reference: (19).
Recovery: 95%. Time Required: ~6 *hr.*

The active portion of the target, about 10 g, is dissolved in HNO_3. After evaporating the solution to dryness, 150 ml of water are added and any insoluble matter is removed by filtration.

Solid NH_4CNS is then added until the precipitate which first forms redissolves. The pH is adjusted to 5 with sodium acetate, and the solution is transferred to a separatory funnel. The Cd^{109} is extracted three times with 50 ml of chloroform containing 50 per cent of pyridine.

The activity is back-extracted into three 25 ml portions of 1 M HNO_3, which are then evaporated to near dryness. The activity is dissolved, treated, and extracted with chloroform–pyridine, as before. After back-extracting into three 25 ml portions of 1 M HNO_3 and evaporation to near dryness, the activity is dissolved in 10 ml of 0·3 N HCl and passed through a Dowex-1 column which has been washed with water and conditioned with 0·3 N HCl.

The column is washed with 6 column volumes of 0·3 N HCl, after which the Cd^{109} is eluted with 0·0003 N HCl. The active eluate is evaporated to near dryness and treated to destroy organic matter. Cd^{109} can be converted to the chloride by evaporation with HCl.

13. *In^{111}.* Target Material: *cadmium.*
Product: 98+% *In activities, in HNO_3 or HCl solution.*
Production Reactions: *$Cd^{110}(d,n)In^{111}$; $Cd^{111}(d,2n)In^{111}$.*
Other Important Reactions: *$Cd^{108}(d,n)In^{109}$; $Cd^{110}(d,2n)In^{110}$; $Cd^{113}(d,n)In^{114}$; $Cd^{114}(d,n)In^{115}$; $Cd^{116}(d,2n)In^{116}$; $Cd^{116}(d,n)In^{117}$.*
Chemical Separation Principles: *Indium activities are carried on $Fe(OH)_3$ from ammoniacal solution. The iron is extracted with isopropyl ether.*
Source Reference: (20).
Recovery: 98% Time Required: ~4 *hr.*

The cadmium target metal, about 10 g, is etched from its backing with HCl. Twenty milligrams of Fe^{III} carrier are added, and the solution is neutralized with NH_4OH. Twenty milliliters of excess NH_4OH are added. The precipitate is separated by centrifugation and dissolved in a minimum of HCl. After diluting to 15 ml with water, the precipitation is repeated. After two additional reprecipitations, 15 ml of 8 N HCl are added, and the iron extracted three times with *iso*propyl ether.

The aqueous phase is evaporated to near dryness. Organic matter is destroyed by repeated evaporations with HNO_3. Conversion to chloride can be effected by evaporation with HCl.

14. *Ce^{139}.* Target Material: *lanthanum oxide.*
Product: 98+% *Ce^{139}, in HNO_3 or HCl solution.*
Production Reactions: *$La^{138}(d,n)Ce^{139}$; $La^{139}(d,2n)Ce^{139}$ or $La^{139}(p,n)Ce^{139}$.*
Other Important Reactions: *none.*
Chemical Separation Principles: *Ce^{139} is extracted into hexone (4-methyl 2-pentanone).*
Source Reference: (21).
Recovery: 95%. Time Required: ~2 *hr.*

The La_2O_3 target, about 3 g, is dissolved in a minimum of 3 N HCl. Five milliliters of HNO_3 are added and the solution is evaporated to dryness. A mixture of 6 ml of HNO_3, 2 ml of 2 M $NaBrO_3$, and 2 ml of water are added, and the resulting solution is cautiously heated until a vigorous reaction ensues. The solution is cooled and transferred to a separatory funnel containing 50 ml of hexone which has been conditioned by shaking with 50 ml of 9 M HNO_3. One milliliter of 2 M $NaBrO_3$ and 1·5 ml of HNO_3 are

added. The funnel is shaken immediately, the phases allowed to separate, and the aqueous layer reserved for further recovery of Ce^{139}. It is important to have excess $NaBrO_3$ present at the time of extraction.

The hexone layer is washed twice with 10 ml of 9 M HNO_3 and a few drops of 2 M $NaBrO_3$. The washes are reserved. Ce^{139} is then extracted from the hexone with two 5 ml portions of water containing 4 drops of 30% H_2O_2. The hexone is discarded into a stream of running water. CAUTION: HNO_3–hexone is potentially explosive.

The residual Ce^{139} in the aqueous phase previously reserved is extracted with hexone, and then the aqueous phase is discarded. The hexone layer is washed twice with 9 N HNO_3 and Ce^{139} is removed from the hexone with two 5 ml portions of water containing 4 drops of 30% H_2O_2. The hexone is discarded.

Since the distribution of Ce^{139} between the hexone and 9 N HNO_3 washes is about 8:1, it is desirable to recover the Ce^{139} in the four washes. These are combined and evaporated to dryness. A mixture of 6 ml of HNO_3, 2 ml of 2 M $NaBrO_3$, and 2 ml of water is added, and the resulting solution heated. The Ce^{139} in the solution is extracted twice with hexone. The hexone layers are each washed twice with 10 ml of 9 M HNO_3, and the washes are discarded. The Ce^{139} in the hexone phases is then back-extracted with two 5 ml portions of water containing 4 drops of 30% H_2O_2.

The H_2O_2 extracts are combined with the first H_2O_2 extracts and are then evaporated to near dryness. Organic matter is destroyed with HNO_3. Conversion to chloride can be achieved by HCl evaporation.

15. W^{181}. Target Material: *tantalum.*
Product: 98+% W^{181}, *in HCl–HF.*
Production Reactions: $Ta^{181}(p,n)W^{181}$ *or* $Ta^{181}(d,2n)W^{181}$.
Other Important Reactions: *none.*
Chemical Separation Principles: *W^{181} is separated from the tantalum by ion exchange. The final separation is accomplished by co-precipitating W^{181} with $Fe(OH)_3$ at pH 4. Iron is extracted with ethyl ether.*
Source Reference: (22).
Recovery: 90+%. Time Required: ~10 *hr.*

The tantalum target is etched with HF in a platinum dish to remove the active layer. About 5 g are dissolved. After evaporating to near dryness, 4 ml of HF and 20 ml of HCl are added, and the mixture is heated to obtain a clear solution. Sixteen milliliters of water are added.

The solution is passed through a 40 cm polyethylene column containing Dowex-1 which has been conditioned with 1·5 N HF + 6 N HCl. W^{181} is eluted with 1·5 N HF + 6 N HCl. Twenty milliliter fractions are collected in polyethylene containers.

The active fractions are combined and evaporated to 5 ml in a platinum dish. Thirty milliliters of water, 200 mg of boric acid, and 10 mg of Fe^{III} carrier are added.

Sufficient 6 N NaOH is added to bring the pH to 4·0. The precipitate which forms is separated by centrifugation and dissolved in a minimum of HCl. The precipitation is repeated twice more. The final precipitate is washed twice with water and dissolved in 6 N HCl.

Iron is extracted three times with ethyl ether. The aqueous phase is evaporated to near dryness. Organic matter is destroyed by evaporation with HNO_3. Conversion to the chloride is effected by evaporation with HCl. One drop of HF is added.

16. Bi^{207}. Target Material: *lead.*
Product: 98+% *Bi activities, in HNO_3 solution.*
Production Reactions: $Pb^{207}(p,n)Bi^{207}$; $Pb^{208}(p,2n)Bi^{207}$.
Other Important Reactions: $Pb^{206}(p,n)Bi^{206}$; $Pb^{207}(p,2n)Bi^{206}$.
Chemical Separation Principles: *The lead is removed by precipitation with fuming HNO_3. Bismuth is co-precipitated with $Fe(OH)_3$ in the presence of an excess of NaOH. Iron is then removed by extraction with ethyl ether.*
Source Reference: (23).
Recovery: ~90%. Time Required: ~6 *hr.*

The lead target metal, about 25 g, is etched from its backing with 6 N HNO_3. After evaporation to about 50 ml, the resulting slurry is transferred to a centrifuge bottle and 100 ml of fuming HNO_3 are added. After cooling in an ice bath, the precipitate is removed by centrifugation, and washed twice with cold fuming HNO_3. Twenty milligrams of Fe^{III} carrier are added to the combined supernate and washes, and the solution is evaporated to near dryness.

Fifteen milliliters of water are added; then 15 ml of 9 N NaOH are added and the mixture stirred. Bismuth is quantitatively carried by the $Fe(OH)_3$, while the soluble plumbate remains in the supernate. The precipitate is separated by centrifugation and dissolved in a minimum of HCl. Three reprecipitations are performed. The final precipitate is dissolved in 15 ml of 6 N HCl, and iron is extracted three times with ethyl ether. Organic matter is removed by evaporation with HNO_3.

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The Determination of Solubility of Difficultly Soluble Compounds with the Aid of Non-isotopic Radioactive Indicators*

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Equations have been established governing the transfer into solution of a microelement during partial dissolution of a solid phase consisting of isomorphous compounds of the micro- and macroelements. A method has been worked out for the determination of solubility of difficultly soluble compounds with the aid of radioactive indicators which are non-isotopic but truly isomorphous with the given compounds, and the effect of the degree of achievement of thermodynamic equilibrium between the whole of the solid phase and the saturated solution upon the character of the curves used for calculating the solubilities has been examined. A method has also been suggested for the determination of solubility of difficultly soluble compounds in solutions containing common ions. The equations obtained have been tested by determinations of solubility of barium sulphate using Sr^{90}, and of potassium chloroplatinate using Cs^{134}.

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ОПРЕДЕЛЕНИЕ РАСТВОРИМОСТИ ТРУДНОРАСТВОРИМЫХ СОЕДИНЕНИЙ С ПОМОЩЬЮ НЕИЗОТОПНЫХ РАДИОАКТИВНЫХ ИНДИКАТОРОВ

Установлены закономерности перехода микроэлемента, истинно изоморфного с соединением макроэлемента, в раствор при частичном растворении твердои фазы, содержащей микроэлемент. Разработан метод определения растворимости труднорастворимых соединений с помощью неизотопных, но истинно изоморфных с данным соединением радиоактивных индикаторов. Выяснено влияние степени достижения термодинамического равновесия между всем осадком и насыщенным раствором на характер кривых, используемых для определения растворимости. Предложен метод определения растворимости труднорастворимых соединений в растворах, содержащих одноименные ионы. Найденные соотношения подтверждены на примерах определения растворимости $BaSO_4$ по Sr^{90} и K_2PCl_6 по Cs^{134}.

LÖSLICHKEITSBESTIMMUNG SCHWERLÖSLICHER VERBINDUNGEN MIT HILFE VON NICHT-ISOTOPEN RADIOAKTIVEN INDIKATOREN

Für die Überführung eines Mikroelementes in Lösung während der Partiallösung der festen Phase, welche aus isomorphen Verbindungen des Mikro- und des Makroelementes

* Translated by G. Ryback from *Atomnaya Energiya* **4**, 354 (1958).

besteht, wurden Gleichungen aufgestellt. Es wurde eine Methode zur Löslichkeitsbestimmung schwerlöslicher Verbindungen ausgearbeitet, und zwar mit Hilfe von radioaktiven Indikatoren, welchezwar nicht isotop, aber streng isomorph mit der vorliegenden Verbindung sind, und der Effekt des Grades der Herstellung eines thermodynamischen Gleichgewichtes der festen Phase und der gesättigten Lösung auf den Charakter der zur Berechnung der Löslichkeiten verwendeten Kurve wurde untersucht. Ausserdem wurde eine Methode zur Löslichkeitsbestimmung schwerlöslicher Verbindungen in Lösungen vorgeschlagen, welche gemeinsame Ionen enthalten. Die gewonnen Gleichungen wurden überprüft durch Löslichkeitsbestimmungen an Bariumsulphat mit Hilfe von Sr^{90} und an Kaliumchlorplatinat mit Hilfe von Cs^{137}.

In the paper by Korenman *et al.*[1] a new method is put forward for the determination of solubility of difficultly soluble compounds with the aid of radioactive indicators which are non-isotopic but truly isomorphous with the given compounds. Their work does not contain sufficiently convincing data in favour of such a method. On the contrary, there is a nearly four-fold disagreement in the values of solubility of cadmium tetrarhodanomercurate determined with the aid of Cd^{115} (isotopic indicator) and Zn^{65} (non-isotopic indicator), which cannot be accepted as satisfactory. Korenman *et al.* base their work on the following suppositions: (i) during the process of saturation of the solution, thermodynamic equilibrium is not reached between the whole of the solid phase and the saturated solution; (ii) the ratios of macroelement to microelement in both phases are equal. If the first supposition is accepted, the second is justified only when the macro- and microelements are isotopes.

If isomorphous compounds of two elements are selected as components of a system, the condition for thermodynamic equilibrium is given by the following relation:[2]

$$\frac{x}{y} = D\frac{(1-x)}{(1-y)} \qquad (1)$$

where x, y, and $(1-x)$, $(1-y)$ are respectively the amounts of microelement and macroelement in the solid phase and in the solution, and D is the coefficient of crystallization.

Let us examine the case in which a compound containing an isomorphous compound of the radioactive indicator is used for saturating the solution. If B denotes the amount of macroelement taken, and the amount of microelement contained is $A = kB$, we obtain from equation (1):

$$\frac{A-a}{B-b} = D\frac{a}{b} \qquad (2)$$

where a and b are the amounts of micro- and macroelements, respectively, in the solution. Assuming that $B = nb$,

$$a = \frac{knb}{D(n-1)+1} \qquad (3)$$

where $n \geqslant 1$.

It follows from equation (3) that the amount a of microelement in the solution depends upon n and D. Analysing equation (3), we find that: (i) when $D > 1$ and $n > 1$, $\frac{a}{b} < \frac{A}{B}$, (ii) when $D < 1$ and $n > 1$, $\frac{a}{b} > \frac{A}{B}$; (iii) when $D \neq 1$ and $n = 1$, $\frac{a}{b} = \frac{A}{B}$; (iv) in the special case when the two elements are isotopes and $D = 1$, $\frac{a}{b} = \frac{A}{B}$ when $n \geqslant 1$. Therefore the calculated value of solubility will be identical with its actual value only in cases (iii) and (iv). Case (iii) is of special interest, since the curve $a = f(n)$, extrapolated to $n = 1$, will give a value of a which can be used for calculating the true solubility of the compound.

In this connexion it is first necessary to decide whether a linear extrapolation of the curve given by equation (3) is admissible in the region of values of n near unity. Substituting $m = n - 1$ in (3) we obtain:

$$a = \frac{kb(m+1)}{Dm+1} \qquad (4)$$

where $m \geqslant 0$. Clearly, when $Dm \ll 1$,

$$a \approx kb[m(1 - D) + 1] \quad (5)$$

from which it follows that the absolute error is

$$[\Delta a]_{\text{abs}} = \frac{kb(m + 1)}{Dm + 1} - kb[m(1 - D) + 1]$$

$$= kb\left[\frac{Dm^2(D - 1)}{Dm + 1}\right] \quad (6)$$

Hence the relative error is

$$[\Delta a]_{\text{rel}} = \frac{Dm^2(D - 1)}{m + 1} \quad (7)$$

It is evident that, provided the condition $Dm \ll 1$ is fulfilled, the error arising out of the approximation of the curve given by equation (4) can be neglected. Moreover, the region of linear extrapolation is extended when D approaches unity.

To test the equations derived above, the solubility of potassium chloroplatinate in water has been determined using radio-caesium.

Determination of solubility of potassium chloroplatinate in water, using radio-caesium

According to data in the literature, chloroplatinates of potassium and caesium are isomorphous.[3,4] The solubilities at 20°C and 30°C, respectively, expressed in g/100 g of water, are:[5] potassium chloroplatinate, 0·7742 and 1; caesium chloroplatinate, 0·0086 and 0·0119. Hence the coefficient of crystallization of caesium in the system K_2PtCl_6–Cs_2PtCl_6 is much greater than unity.

We have prepared potassium chloroplatinate containing Cs^{134} as indicator by the action of a solution of chloroplatinic acid (H_2PtCl_6) on potassium nitrate solution containing radio-caesium. For the determination of solubility of potassium chloroplatinate, small portions of the prepared salt were weighed out into ampoules to which a constant volume of water (3 ml) was added, and which were then sealed. Preliminary experiments showed that when the ratio of solid to liquid was small, the saturation of the solution was achieved after shaking the bulbs mechanically for 1–2 hr. To ensure saturation of the solution, all the ampoules were shaken simultaneously at 28°C for 6 hr, after which samples of the solutions were taken for radioactivity measurements.

The results are represented graphically in Fig. 1. As can be seen from the graph, there is a linear increase of activity in the region of unsaturated solutions, when the solid phase has dissolved completely (curve 1). In the

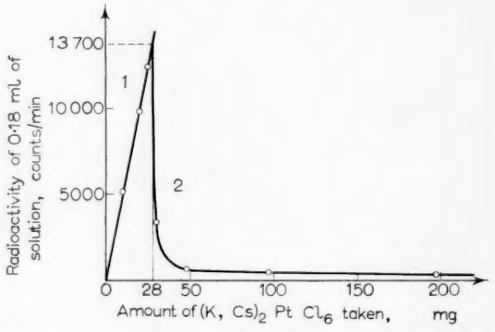

FIG. 1. Determination of solubility of potassium chloroplatinate in water, using radio-caesium.

presence of solid, the activity of the solution falls according to equation (3) for $D > 1$ (curve 2). We have extrapolated curve 2 to its intersection with the straight line 1. The point of intersection corresponds to the value of a when $n = 1$, from which it is easy to calculate the solubility of potassium chloroplatinate, knowing the specific activity of the salt.

The solubility of potassium chloroplatinate at 28°C was found to be 0·93 g/100 ml which agrees with the published data.

In these experiments thermodynamic equilibrium between the solid phase and the solution had not been reached. It is therefore necessary to examine the effect of the degree of achievement of such an equilibrium upon the character of the curve used for calculating the solubility.

Effect of the degree of achievement of a state of equilibrium between the whole of the solid phase and the solution upon the character of the curve used for calculating solubilities

As indicated above, equation (3) is based on the supposition that equilibrium has been reached between the whole of the solid phase and the solution. In cases where equilibrium

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is reached only between a part of the solid and the solution, equation (3) takes the form

$$a = \frac{kbin}{D(in - 1) + 1} \qquad (8)$$

where the coefficient i shows the degree of interaction of the solid phase with the solution. It follows from equation (8) that a closer approximation to equilibrium must be expressed by a sharper curvature of the plot of the radioactivity of the solution against the amount of solid. To test this, experiments were carried out to determine the solubility of barium sulphate in water, using Sr^{90}, after varying times of contact of the phases.

According to data in the literature[3] sulphates of barium and strontium are isomorphous, but the solubility of barium sulphate is much lower than that of strontium sulphate. The solubilities expressed in g/l. of solution are:[6] barium sulphate, 0·00246 at 25°C, strontium sulphate, 0·114 at 30°C. Hence the coefficient of crystallization of strontium in the system $BaSO_4$–$SrSO_4$ should be much smaller than unity.

The solid $(Ba,Sr)SO_4$ was prepared by mixing a solution of barium chloride containing Sr^{90} with an excess of sulphuric acid. For recrystallization, the precipitate was left overnight in contact with the mother-liquors, after which it was washed thoroughly with water, dried at 100°C, and used in the solubility determinations. To find the specific activity of the precipitate, the radioactivity of a small sample (0·23 mg) was measured under conditions identical with those used later for measurements on samples of solution. The amount of $(Ba,Sr)SO_4$ taken in each experiment varied, whereas the volume of water was 50 ml in every case. The prepared suspensions were shaken mechanically at 28°C. After 12 and 24 hr, samples of the solutions were taken, but their radioactivity was measured after 15 days, i.e. after radioactive equilibrium between Sr^{90} and Y^{90} had been reached.

The results are represented graphically in Fig. 2, in which curve 1 (corresponding to 12 hr of contact of the phases) when extrapolated is found to coincide with curve 2 (corresponding to 24 hr of contact). From this we conclude that in both cases a state of saturation of the solution had been reached. The sharper curvature of curve 2 indicates more complete interaction of the phases, and

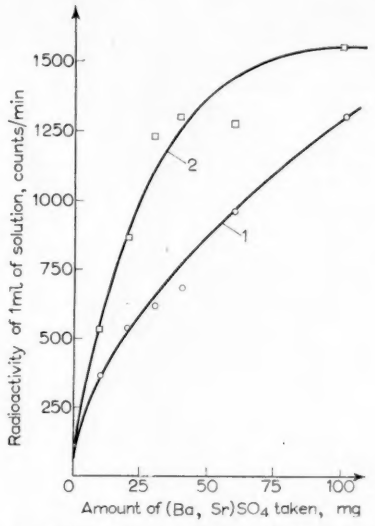

FIG. 2. Effect of the degree of interaction between $(Ba,Sr)SO_4$ and the solution upon the character of the curve used for calculating solubilities.

therefore a higher value of the coefficient i.

The value of a when $n \approx 1$ can be determined from these results, and since the specific activity of the $(Ba,Sr)SO_4$ is known, the solubility of barium sulphate can be calculated. We have found the solubility at 28°C to be 0·0026 g/l. ±25 per cent, which agrees with the published data.

Determination of solubility of a salt in the presence of common ions

Calculations have shown that the non-isotopic radioactive indicator method can be used to determine the solubility of a salt in the presence of common ions. A state of thermodynamic equilibrium between the solid phase and the solution is defined by the relation

$$\frac{A - a}{B - b} = D\,\frac{a}{b(q + 1)} \qquad (9)$$

where qb is the amount of macroelement in the solution in the form of other salts.

RATNER[7] and POLESSITSKY[8] have established that

$$D = D_0\left(\frac{\gamma}{\gamma'}\right)^{\nu} \qquad (10)$$

where D_0 is the true coefficient of fractionation, γ' and γ are activity coefficients of the salts of macro- and microelements in solution, and ν is the number of ions formed by dissociation of the salt under consideration. From (9) and (10) we obtain

$$a = \frac{knb}{D_0\left(\frac{\gamma}{\gamma'}\right)^{\nu}(n-1)/(q+1)+1} \qquad (11)$$

Equation (11) is clearly analogous to equation (3). To test equation (11) the solubility of potassium chloroplatinate in 0·1 N and 0·2 N potassium chloride has been determined using radio-caesium. For this purpose the same $(K,Cs)_2PtCl_6$ precipitate was employed as that used for determining the solubility of this salt in water, and the method was analogous. The time of contact of the solid with the solution was 6 hr, from which it is supposed that the values of the coefficient i were closely similar in all the experiments.

Fig. 3 shows graphically the function $a = f(n)$ for solutions of $(K,Cs)_2PtCl_6$ in water (curve 1) and in 0·1 N and 0·2 N potassium chloride (curves 2 and 3, respectively), the condition $a_{n=1} = 1$ being assumed for each curve. As the concentration of potassium chloride in the solution increases, the value of

$$\frac{D_0\left(\frac{\gamma}{\gamma'}\right)^{\nu}}{q+1}$$

in relation (11) decreases, this being accompanied by a change in the curves of the function $a = f(n)$ shown in Fig. 3. Moreover, Fig. 3 shows that when the value of

$$\frac{D_0\left(\frac{\gamma}{\gamma'}\right)^{\nu}}{q+1}$$

approaches unity, the accuracy of the determination of solubility of the salt is greater.

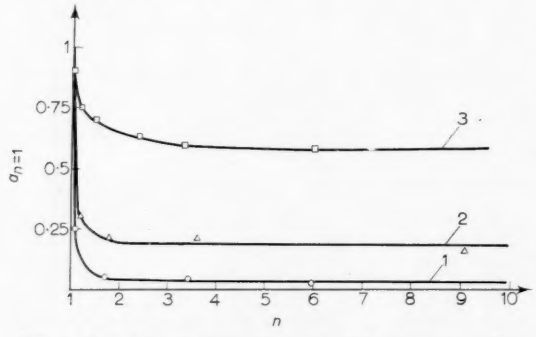

FIG. 3. Dependence of the character of the curves $a = f(n)$ upon the concentration of common ions in the solution.

The solubility of potassium chloroplatinate in 0·1 N and 0·2 N potassium chloride solutions at 28°C was found to be 0·110 g and 0·033 g/100 ml of solution, respectively. According to the literature[5] the solubility of potassium chloroplatinate in 0·2 N potassium chloride solution at 20°C is 0·0236 g/100 ml.

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Labeling Surfaces with Radioactive Gases

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A radiochemical technique has been developed by means of which specific elements on a surface can be selectively labeled. The technique involves selective chemical reactions between one element of interest and a radioactive gas to form a radioactive compound. Autoradiography is then used to determine the distribution of the compound on the surface. The technique has been successfully applied to the location of imperfections in coatings by choosing a radioactive gas which reacts with unprotected areas but not with the coating material. Results obtained with two systems, TiO_2 coatings on aluminum and chrome plate on stainless steel, are described. Experimental techniques, sources of error, and advantages and limitations of the method are discussed.

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LE MARQUAGE DES SURFACES AU MOYEN DES GAZ RADIOACTIFS

Une technique radiochimique a été développée pour le marquage sélectif d'éléments déterminés sur une surface. La technique comprend des réactions chimiques sélectives entre un élément intéressant et un gaz radioactif pour produire un composé radioactif. L'autoradiographie sert alors à présenter la distribution du composé formé sur la surface. La technique s'est prêtée avec succès à repérer les imperfections dans des couches, grâce au choix d'un gaz radioactif qui réagit avec les parties non protégées et non pas avec la substance de la couche. On décrit les résultats donnés par deux systèmes, des couches de TiO_2 sur l'aluminium et de l'acier inoxydable plaqué de chromium. On discute les techniques expérimentales, les origines d'erreur, les avantages et les limitations de la méthode.

MARKIERUNG VON OBERFLÄCHEN MIT RADIOAKTIVEN GASEN

Es wurde ein radiochemisches Verfahren entwickelt mit dessen Hilfe gewisse Elemente auf Oberflächen selektiv markiert werden können. Dieses Verfahren beruht auf der selektiven chemischen Reaktion welche zu radioaktiven Verbindungen zwischen dem in Frage kommendem Element und dem radioaktiven Gas führen. Hierauf wird die Verteilung dieser Verbindungen auf der Oberfläche mittels Autoradiographie bestimmt. Das Verfahren wurde bereits mit Erfolg zur Auffindung von Fehlern in Schutzschichten verwendet, wobei ein radioaktives Gas gewählt wurde, welches nicht mit dem Material der Schutzschichte, jedoch mit dem unbedeckt darunter liegenden Material chemisch reagiert. Resultate welche bei TiO_2 auf Aluminium und mit Chrom auf rostfreiem Stahl erhalten wurden, werden beschrieben. Die technische Durchführung, Fehlerquellen, Vorteile und Grenzen der Methode werden diskutiert.

INTRODUCTION

In recent years radioactive tracers have been used extensively to gain information about metal surfaces. This use of tracers has greatly extended the amount of information obtainable. Various tracer techniques have been applied depending on the nature of the particular problem being investigated. For example, Richmond *et al.*[1] studied the distribution of a nickel coating by adding radioactive nickel to the material used for coating. Wolff *et al.*[2] approached a similar problem by making a thin layer of the base metal radioactive. Verkerk[3] studied the distribution of copper in a silver–copper alloy by using isotopic exchange from solution to make the copper radioactive. A number of other tracer experiments have been reported, many of which are described by Simnad.[4,5,6]

Although several workers have used radioisotopes of elements not present in the materials under test in such studies as gas adsorption,[7] differences in surface potential[8,9] and friction,[10] most experimenters have utilized a radioactive isotope of one of the elements in the system. Frequently, however, it is desirable to use a tracer technique with a system where there is no suitable tracer available for any of the elements present. This paper describes a technique which can be applied in such a situation. Briefly, the technique involves the use of a radioactive gas which undergoes a selective chemical reaction with one of the elements in a system of interest to form a radioactive compound. The distribution of the compound is then determined by autoradiography.

This approach has many advantages over other tracer techniques. It can be applied more widely, it is capable of excellent resolution, and eliminates many handling problems. The technique appeared to be particularly suited to the location of imperfections in coatings; therefore, it was first applied to two groups of coated materials.

EXPERIMENTAL

The two systems studied were thin TiO_2 coatings on aluminum and thin chrome plate on stainless steel. In each case radioactive sulfur dioxide, containing S^{35}, was used as the labeling gas. Foley[11] has shown that in the presence of moisture sulfur dioxide will attack aluminum uniformly with the formation of a water-soluble compound. Mears and Evans[12] have observed similar corrosion of iron by sulfur dioxide and water. Both TiO_2 and chromium, however, are resistant to such attack. Thus, it is possible to locate uncoated areas by exposing the samples to radioactive sulfur dioxide and then locating areas of radioactivity by autoradiography.

The radioactive sulfur dioxide, in a glass ampoule,* was sealed into a sampling apparatus as shown in Fig. 1. Using this apparatus a small fraction of the gas can be withdrawn for use in each experiment.

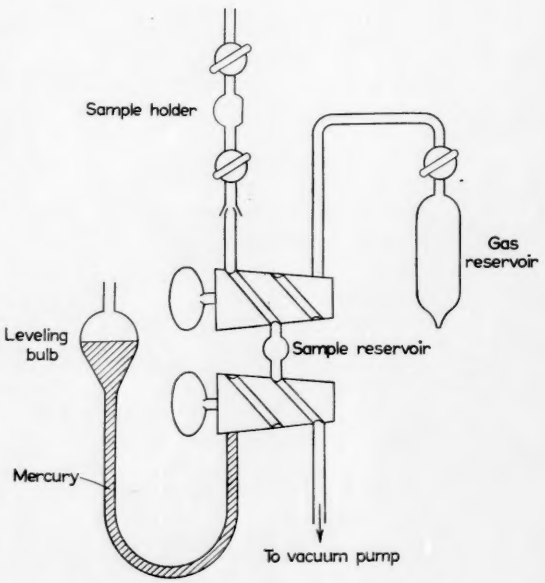

Fig. 1. Gas sampling apparatus.

* Obtained from Volk Radiochemical Company.

The experimental procedure followed with each group of samples is as follows.

The samples were cleaned with carbon tetrachloride to remove any residual dirt or grease and then placed in a bell jar. A vacuum was drawn and water-vapor introduced into the chamber. Radioactive gas was then introduced into the chamber, still at a pressure slightly below atmospheric. It is estimated that approximately 100 μc of S^{35} were present in each exposure. This corresponds to about 0.02 mmole of sulfur dioxide since the specific activity of the gas was 5 mc/mmole. These samples were left in the chamber overnight to allow as much as possible of the sulfur dioxide to react. The resulting high concentration of radioactivity on the samples assures that a satisfactory autoradiograph can be achieved with a film exposure of about an hour. Less active samples frequently require many days in contact with film before a detectable image is formed. When the bell jar was opened after exposure of the samples, no appreciable radioactivity could be detected in the air of the hood, indicating that the reaction was essentially complete. After removal from the bell jar, the samples were placed in a light-tight container in contact with Kodak Type AA X-ray film until a good image was obtained. As stated above, this required approximately one hour.

RESULTS

A. TiO_2–Aluminum

The first system studied was that of aluminum coated with TiO_2. The coating was applied as a titanium resinate paint* and the samples were baked at about 700°F to drive off the volatile material in the paint. The first experiments were performed using samples which were purposely only partially coated with TiO_2 as a check on the method. Fig. 2A shows an autoradiograph of a group of these samples. The upper two samples are uncoated aluminum controls, while the lower two samples are coated with strips of TiO_2. Fig. 2B shows an ordinary photograph of these samples. The black areas on the autoradiograph correspond to uncoated aluminum which has been attacked by the radioactive sulfur dioxide. In the areas which have been coated with TiO_2 no reaction has occurred and thus no radioactivity is present. Thus these areas on the autoradiograph are white. In the lower right hand sample, the coating appeared to have partially flaked off and this was verified in the autoradiograph by the observance of radioactivity in the suspected region.

The method thus seemed to give an excellent picture of the degree of perfection of the coating. Experiments were next performed on test samples which had been coated by various methods. Results obtained with two of these are shown in Figs. 3 and 4. Obviously the coating shown in Fig. 3 is much more satisfactory than that in Fig. 4, although both contain many imperfections. The black areas in the autoradiographs can be correlated rather well with visual imperfections in the coatings and show also the presence of additional imperfections which cannot be detected visually.

B. Chrome plated steel

This same procedure was applied to the examination of various thin chrome plates on stainless steel. An autoradiograph obtained from a group of these samples is shown in Fig. 5. The ends of the samples, being unplated, have become quite radioactive and pinholes can be observed throughout the plated portion of the samples. Sample H-18 was evidently covered by a very porous plate since a general reaction with the radioactive sulfur dioxide took place over the entire surface. Sample H-6 contained large areas where the plate had peeled off and these correspond to the very black areas on the autoradiograph.

* Dupont.

DISCUSSION

A. Resolution

The resolution of the method is limited at least in part by the type of photographic emulsion used. Kodak Type AA X-ray film was used in most of this work because it is relatively fast and very high resolution was not required. Somewhat higher resolution can be obtained using Dupont Type 506 (Fine Grain) X-ray film or Dupont Type 510 (Very Fine Grain) X-ray film. Use of these finer grain films requires somewhat longer exposure times than does Type AA. The stripping film technique described by Boyd[13] and by Pelc[14] is capable of very high resolution, but presents many more experimental problems. Its use is therefore recommended only in those cases where the increased resolution is absolutely necessary.

The X-ray films used in this work are all double emulsion films and if any radioactive particles should penetrate through to the second emulsion, the autoradiograph would suffer losses in resolution. However, the β-particles emitted by S^{35} have such a low kinetic energy that none penetrate to the second emulsion.

If a large amount of sulfur dioxide were permitted to attack the samples, reaction could occur to an appreciable depth below the metal surface and radioactivity would thus be present in the sample at significant distances from the surface. This would lead to losses in resolution in the autoradiograph as a result of scattering of radiation before it reached the photographic emulsion. However, as previously stated, only a very small total amount (approx. 0.02 mmole) of sulfur dioxide was present in the exposure chamber during these experiments. Thus, only the surface of the sample could be attacked before the gas was consumed. From Geiger counter measurements of the radioactivity present, the depth of penetration has been calculated to be of the order of a few microns. This is too short a distance so cause significant losses in resolution for this work.

B. Sources of error

Serious errors in interpretation of autoradiographs could result if significant adsorption of sulfur dioxide by either the TiO_2 film or the chrome plate occurred. The preliminary experiments using partially coated samples were designed to evaluate the extent of this interference. It was found that when samples were placed in the exposure chamber without any precleaning, sulfur dioxide was adsorbed on the TiO_2 coated areas as well as on the bare aluminum. This was probably due to dirt or residual organic materials remaining from the coating application since samples cleaned in CCl_4 prior to placing in the exposure chamber did not show this effect.

C. Limitations

The major limitation on the use of this technique is that of finding a radioactive gas which will undergo a chemical reaction with one and only one component of the system under study. The two systems involved in this work were relatively simple and it was possible to choose a selective chemical reaction without much difficulty. Many different radioactive gases are available, for example, CO_2, CO, H_2S, H_2, etc., and it should be possible to choose at least one which will give the desired result with almost any system.

D. Comparison with other tracer techniques

As previously stated, the technique described in this paper has a special advantage in that it can be applied to systems where radioactive isotopes are not available for any of the elements present. In addition, with this technique no synthetic materials incorporating tracers need be prepared. Commercially available material can be evaluated directly. This has two advantages. First, the problem of duplicating exactly in a synthetic, tracer-containing material the effects of various pretreatments which a commercially available material may have received is eliminated, and second,

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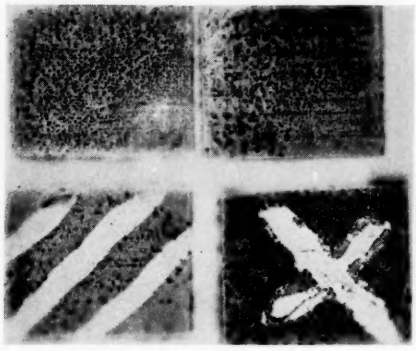
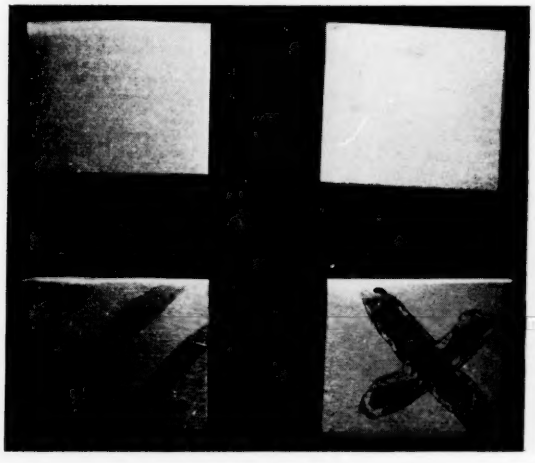
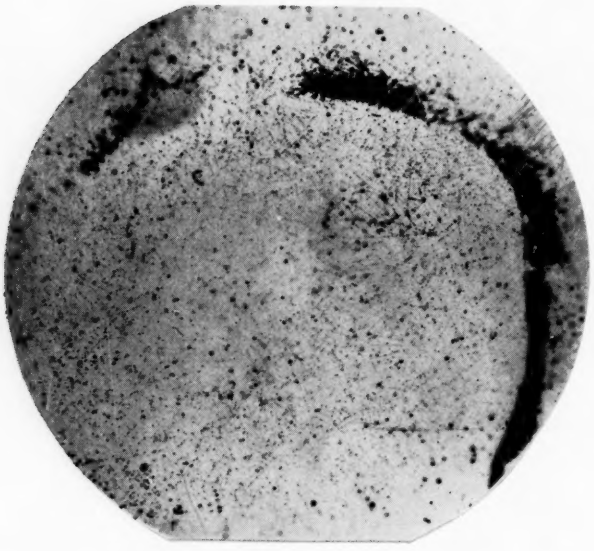


A. Autoradiograph

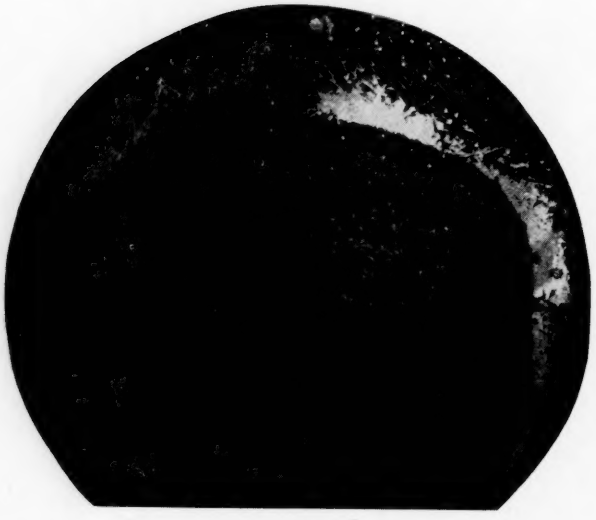


B. Photograph

FIG. 2. Aluminum samples partially coated with TiO_2 and exposed to radioactive SO_2.



A. Autoradiograph



B. Photograph

FIG. 3. Aluminum sample coated with TiO_2 and exposed to radioactive SO_2.

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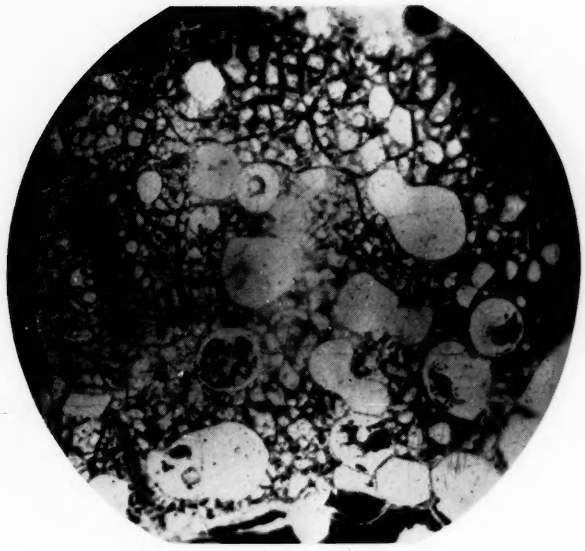
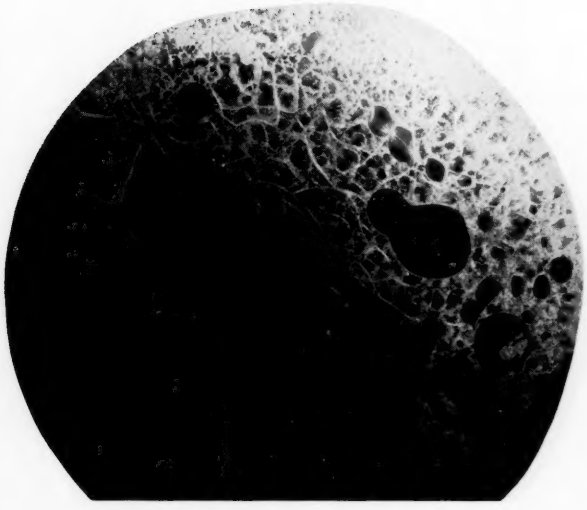


A. Autoradiograph



B. Photograph

FIG. 4. Aluminum sample coated with TiO_2 and exposed to radioactive SO_2.

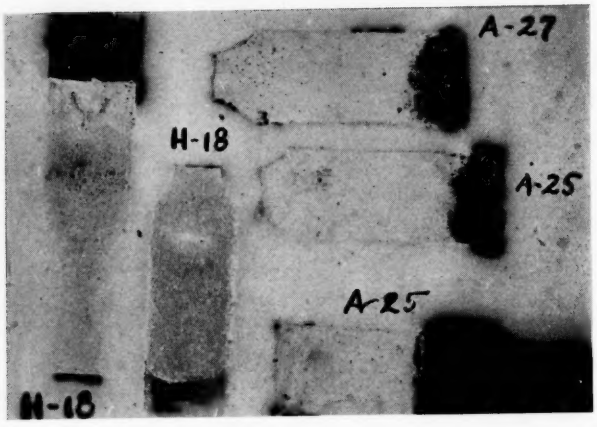


FIG. 5. Autoradiographs of chrome-plated stainless steel after exposure to radioactive SO_2.

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the problem of handling large amounts of radioactivity during the coating or other experimental operations is also eliminated. Handling problems are simplified even further since when the tracer is finally added to the system, only very small amounts of radioactivity become associated with the samples.

Also, in coating studies, if the entire piece of substrate material is made radioactive prior to coating, losses in resolution will occur in the autoradiograph due to scattered radiation from below the surface as discussed under heading *A*. WOLFF *et al.*[2] have overcome this very well in the case of nickel coatings on steel by plating a very thin layer of radioactive iron onto the steel prior to coating. However, this method could not be applied to the TiO_2–aluminum system since no tracer is available for aluminum. It would also be difficult to apply this method to the study of very thin coatings where the radiation emitted by the substrate layer may be energetic enough to penetrate the coating. These problems can be overcome by using a tracer in the coating rather than the substrate; however, this is not always experimentally feasible or, as in the case of titanium, may even be impossible.

A labeling technique using radioactive solutions applied by RABINOWICZ[10] to friction studies has similar advantages to the gas labeling technique. However, in cases where immersing samples in solutions must be avoided, it may still be possible to utilize gas labeling.

CONCLUSIONS

Utilizing the chemical reactions between aluminum and radioactive SO_2, imperfections in a thin TiO_2 film on aluminum can be located even though they are not apparent under visual inspection. The same technique can be used to locate imperfections in thin chrome plate on stainless steel. The basic technique can be applied to many different systems by utilizing the many different radioactive gases available. Different degrees of resolution can be achieved by choosing the proper combination of experimental conditions. Interferences such as adsorption must be kept to a minimum to eliminate errors in interpretation of autoradiographs. Handling of large amounts of radioactive materials is kept to a minimum since:

(1) no radioactivity is introduced until after the sample treatment has been completed, and
(2) the radioactivity is confined to a thin surface layer.

The technique can be used with systems where radioactive isotopes are not available for any of the elements present and has definite advantages over many other labeling techniques.

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A Machine for the Automatic Chromatography and Assay of Mixtures of Radioactive Substances

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The construction and operation of a machine, used for the automatic chromatography and estimation of mixtures of radioactive substances, are described. The apparatus is designed to collect effluent fractions of equal volume from a chromatographic column, evaporate them to dryness, count them in turn beneath an end window G.M. counter and provide a record of the counts obtained. Some typical results are given, and the performance and versatility of the machine are discussed.

UNE MACHINE POUR LA CHROMATOGRAPHIE AUTOMATIQUE ET POUR LE DOSAGE DE MÉLANGES DE MATIÈRES RADIOACTIVES

On décrit la construction et le fonctionnement d'une machine servant à la chromatographie automatique et au dosage de mélanges de matières radioactives. L'appareil est destiné à recevoir d'une colonne chromatographique des portions de l'effluent de quantité fixe, à les faire évaporer à sec, à les compter à tour de rôle sous un compteur Geiger ayant la fenêtre au bout, et à enregistrer les comptes ainsi obtenus. On donne quelques résultats typiques, et on discute l'exécution et les capabilités variées de la machine.

EINE MASCHINE ZUR AUTOMATISCHEN CHROMATOGRAPHIE UND MESSUNG VON GEMISCHEN RADIOAKTIVER SUBSTANZEN

Die Konstruktion und das Funktionieren einer Maschine werden beschrieben, welche für automatische Chromatographie und zur Bestimmung von Gemischen radioaktiver Substanzen verwendet wird. Der Apparat sammelt ausfliessende Fraktionen gleichen Volumens von einer chromatographischen Säule, verdampft sie bis zur Trockenheit, zählt sie der Reihe nach unter dem Fenster eines Geiger Müller Zählers und liefert die erhaltenen Messresultate auf einem Schreiber. Einige typische Resultate werden angeführt. Das Funktionieren und die vielseitige Verwendungsfähigkeit der Maschine werden diskutiert.

When a mixture of radioactive substances is analysed by column chromatography, the effluent from the column is usually cut into successive fractions which have then to be prepared for counting. In work involving the separation and estimation of the p-iodobenzenesulphonyl derivatives of amino acids labelled with I^{131},[1] large numbers of such fractions had to be quantitatively transferred from the collecting tubes, evaporated on aluminium trays, stored in a definite order, and counted. The manipulations involved were both laborious and time consuming. The apparatus described here was designed to carry out this procedure automatically and consists essentially of a fraction cutter with built-in heaters, which collects and evaporates fractions on small

metal trays, together with timing, counting, scaling and recording equipment. Novel features of the equipment include a small capacity pump which delivers organic solvents at a constant rate, arrangements for automatically adjusting heater wattage to correspond with the changing composition of the solvent in gradient elution chromatography, loading and unloading mechanisms for the trays and a recording unit which scans the electrodes of the bank of Dekatron tubes on which the count is displayed and prints out the result. The apparatus comprises a turntable unit, a scaling unit and a recording unit, all of which are operated at preset time intervals by a timing unit. A block diagram of the equipment is shown in Fig. 1 and a photograph in Fig. 2.

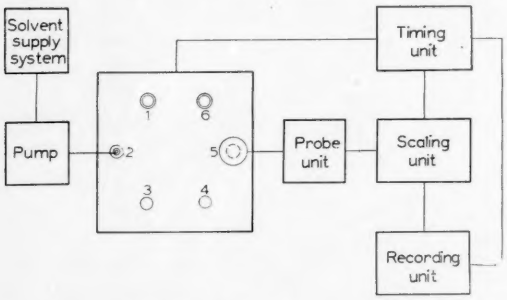

FIG. 1. Block diagram of the apparatus.

As the turntable unit is operated at regular time intervals, equal volumes of effluent are collected by maintaining a constant flow of solvent through the chromatographic column. This is achieved by a constant displacement pump working between a solvent supply system, of a type determined by the chromatographic requirements, and the column. The type of pump used depends on the nature of the solvents employed. Peristaltic pumps, employing rubber tubing,[2] can be used for acidic solvents, but a specially constructed metal pump[3] has been found to be more generally applicable, especially with organic solvents or when appreciable pressure differences have to be overcome. Two metal diaphragm pumps connected in parallel and working out of phase are controlled through a common slide-valve mechanism to give a continuous flow of solvent. The flow rate can be adjusted from 2 to 14 ml/hr as required.

Turntable unit

This part of the instrument collects liquid fractions from a chromatographic column, evaporates them to dryness and presents them to a Geiger counter for measurement of their radioactivity. The fractions are carried in dish-shaped aluminium trays which are fitted into specially shaped anodized aluminium alloy planchettes (Fig. 3). The latter are transported in holes in a six station turntable.

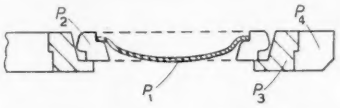

FIG. 3. Section through turntable showing planchette and tray.
*P*1 Tray
*P*2 Planchette
*P*3 Asbestos insert
*P*4 Turntable

At the first station, planchettes are loaded on the turntable from a supply magazine. At the second station, trays receive liquid from the chromatographic column and are simultaneously heated to remove some of the solvent by evaporation. Solvent remaining in the trays is removed by another heater at the next station. A fourth station is present to allow the planchettes and trays to cool. At the next station, the activity on the trays is measured for a preset time under the end window of a Twentieth Century Electronics, type EW3H, Geiger–Müller counter housed in a 1·5 in. thick lead castle, which also supports the probe unit. Finally, at the sixth station, active trays are ejected in their planchettes to a storage magazine.

Each time the unit is energized a shaft turned at the rate of 20 rev/min by a geared, synchronous motor, is arranged to complete exactly one revolution by means of a cam-operated micro-switch. This motion is transmitted through a Geneva mechanism

(Fig. 4: *T*1) with a six-slotted wheel to an aluminium alloy turntable (*T*2) with six equally spaced, asbestos-lined holes, housing the planchettes and their trays. The Geneva mechanism is such that for two-thirds of a revolution of the driving shaft the turntable is at rest. The loading on and removal of planchettes take place during this interval. A cam (*T*3) on the driving shaft causes a plunger to lift momentarily and push the used planchette up through a pair of spring-loaded retaining jaws (*T*4) into the storage magazine (*T*5). Simultaneously another cam (*T*6) causes two pairs of lever controlled jaws (*T*7), situated beneath the supply magazine, to open and close consecutively allowing one planchette to fall into the empty hole in the turntable. The sides of the hole and planchette are both tapered to ensure that the latter is always accurately aligned.

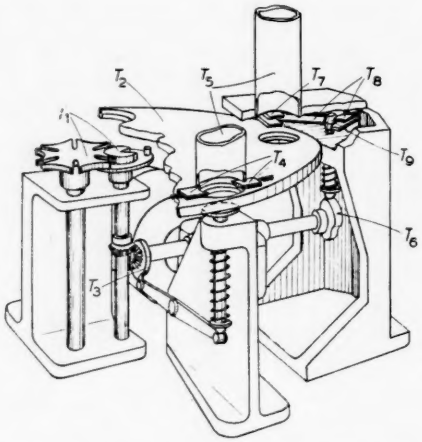

FIG. 4. Cut-away drawing of part of turntable unit.
*T*1 Geneva mechanism
*T*2 Turntable
*T*3 Unloading cam
*T*4 Spring-loaded retaining jaws (unloading)
*T*5 Storage magazines
*T*6 Loading cam
*T*7 Lever controlled jaws (loading)
*T*8 Jaw levers
*T*9 Lever actuator

Manual operation of the turntable motor is controlled by an inching button.

The latent heat of evaporation of the solvent is supplied by two flat spirals of nichrome wire, each sandwiched between two sheets of asbestos paper, and mounted close to the underside of the planchettes. They provide heat at a relatively low temperature with a maximum combined dissipation of 50 W.

The evaporation procedure must be carried out at the correct rate. If the heater wattage is too high, boiling of the solvent occurs and the turntable becomes contaminated with radioactivity. On the other hand, too low a wattage also gives rise to contamination through flooding. Difficulty arises when solvents are continually changing in composition since the heater wattage must also vary to ensure correct evaporation. This is overcome by controlling the output of the heater by means of a specially wound potentiometer in the primary circuit of the heater transformer. Each time the turntable is indexed its motion is transmitted through a chain drive (Fig. 5: *H*1), a friction wheel (*H*2) and disc (*H*3) and a train of gears, to rotate the potentiometer wiper-arm (*H*4) through any angle from 0° to 6°. Thus, during a chromatogram the heater wattage can be held constant, or automatically gradually increased or decreased, by suitable adjustment of the initial setting of the potentiometer wiper-arm, and the position of the friction drive disc on the wheel. These adjustments are made by two controls (*H*5, *H*6) fitted with circular reference scales for easy and reproducible manipulation. With correct heater settings it is possible to control the evaporation so that never more than about three drops of solvent accumulate in a tray. The two stations at which evaporation of solvent takes place are covered by a metal hood which is connected to a small built-in centrifugal extractor fan, to remove noxious fumes.

A rotating shutter, geared to the turntable, moves under the discharging tip of the chromatographic column every time the turntable rotates. A drop of liquid falling at the moment when no tray is under the tip is caught on the shutter and prevented from contaminating the turntable. With fast flowing columns this precaution is

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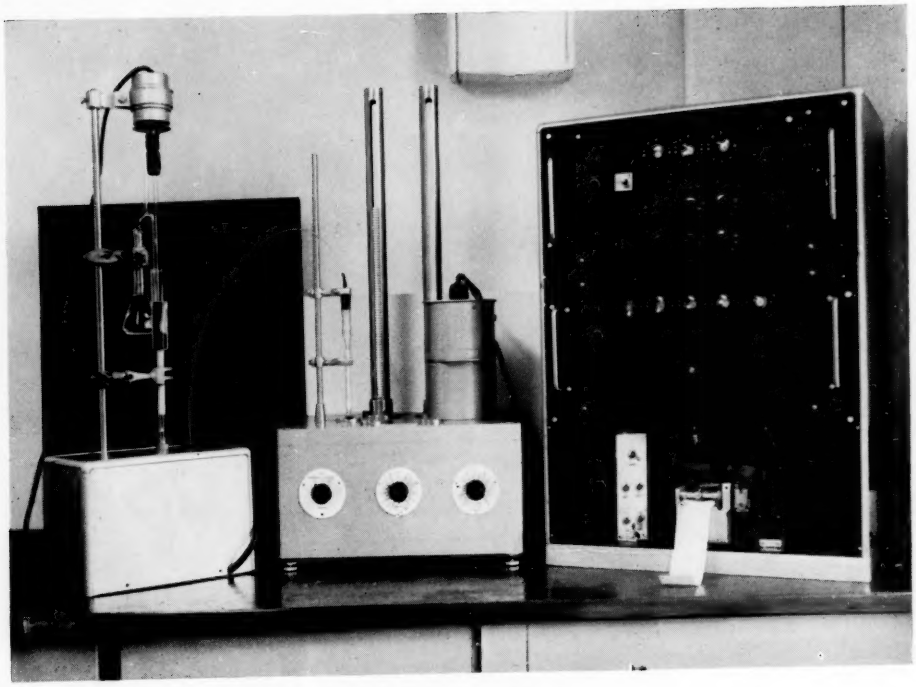

FIG. 2. General view.

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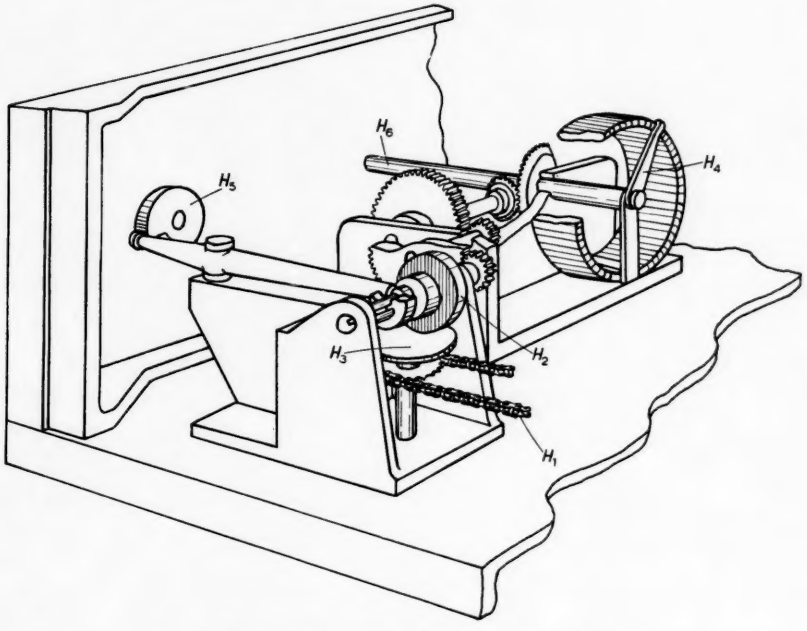

FIG. 5. Cut-away drawing of heater control mechanism.

*H*1	Chain drive	*H*4	Potentiometer wiper-arm
*H*2	Friction wheel	*H*5	Initial setting control
*H*3	Disc	*H*6	Potentiometer drive setting control

necessary since it requires about one second for the turntable to move.

Probe unit and scaling unit

The Geiger–Müller tube operates a probe unit of conventional type, having preset dead times of 200, 300, 400 or 500 μsec, which feeds positive-going pulses of about 40 V amplitude to the input circuit of the scaling unit. This is a five decade scaler, employing Dekatron tubes throughout. The first decade utilizes an Ericsson tube type GC10D, the driving circuits of which have a paralysis time of about 40 μsec. The other four decades use the low-speed Dekatron selector tube type GS10C, with a hard valve pulse generator as coupling between first and second stages, and gas-filled trigger tetrodes between subsequent stages. Separate cathode resistors are fitted for each of the ten cathodes of the last four decades, so that when the glow rests on a particular cathode the voltage developed across the cathode resistor can be used to operate the recording unit.

The polarizing voltage for the Geiger–Müller tube (approx. 600 V), is obtained from a voltage doubling rectifier circuit driven from the main supply transformer secondary winding, corona stabilizer tubes being used for filtering and stabilizing.

Recording unit

This machine records the count registered by the scaling unit on recording paper. Use is made of the fact that the operating cathodes of the indicating Dekatrons in the scaling unit are at about plus 40 V relative to earth. The ten cathodes of each Dekatron are connected in turn to the grid of a biased-off valve having a pen-operating relay in its anode circuit. The arrangement is such that the pen is pressed on the paper by this relay only when the valve grid is connected to an operating cathode or to another 40 V supply.

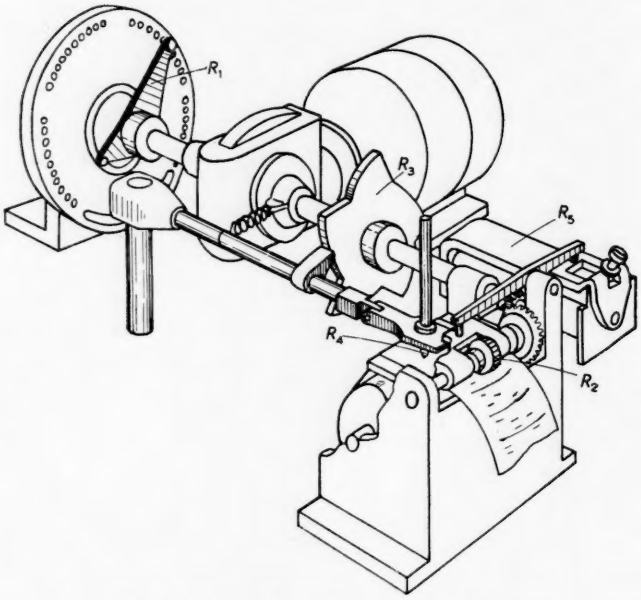

FIG. 6. Cut-away drawing of recording unit.

*R*1	Contact wiper-arm	*R*4	Pen
*R*2	Paper drive roller	*R*5	Pen-relay
*R*3	Five lobe cam		

When the unit is energized, a driving shaft, turned at 6 rev/min by a geared, synchronous motor, is arranged to complete exactly one revolution, by means of a cam-operated micro-switch. This shaft carries an insulated wiper-arm (Fig. 6: *R*1), connected to the grid of the valve, which moves over an insulated bank of four groups of ten short contacts, connected in order to the Dekatron cathodes, and one long contact, maintained at 40 V by means of a small power pack. Only four of the five Dekatrons in the scaler are scanned in this arrangement because the reading of the units Dekatron is of no practical interest. The driving shaft is geared to the paper drive roller (*R*2) and also carries a five lobe cam (*R*3), which causes the pen (*R*4) to traverse the paper. The pen-point is normally clear of the paper but is pressed down on to it when the pen-relay (*R*5) is activated.

When the printing-out unit is energized, the driving shaft turns and drives the wiper-arm, pen and recording paper. The pen on its first journey across the paper draws a continuous line while the wiper-arm engages with the long contact; on each of its next four crossings the pen draws one short line in a position determined by the number indicated by one of the Dekatrons.

The record is removed when the chromatogram is finished and the numbers are read off with the aid of a small transparent graticule (Fig. 7). The record is run through a small machine containing the graticule. Each turn of the handle moves the paper the correct distance to bring the next trace under the graticule; at the same time it indexes a small revolution counter which is set to indicate the number of the corresponding fraction.

Timing unit

All the operations of the equipment are controlled by a master-timer, using Dekatron scaling tubes with trigger tetrode interstage couplings. Pulses derived from the main a.c. supply are divided by 10, 5 and 10 in a three stage scaler to give a basic time interval of 10 sec. Further division by 10,

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10 and 10 is done by three more Dekatron stages, this time using GS10C selector tubes, which have individual cathode pins. These tubes display the elapsed time in tens, hundreds, and thousands of seconds, respectively, up to the maximum value of 9990 sec.

The two basic time intervals required to operate the machine are the loading time, the interval between successive movements of the turntable, and the counting time.

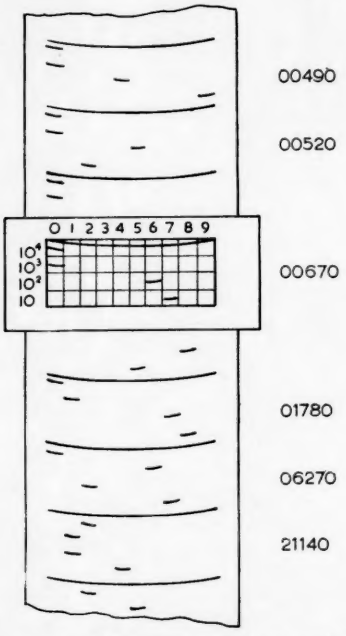

FIG. 7. Portion of recording paper showing method of using graticule.

These times, in units of 10 sec, are set up on two groups of three decade switches.

The action of each group of decade switches is to connect the appropriate cathodes of the three display Dekatrons to a gate circuit which is normally applying negative bias to the grid of a small thyratron. The gate removes this bias, so allowing the thyratron to fire, only when all three cathodes are carrying current, and this occurs when the elapsed time has become equal to the time selected on the switch.

The sequence of events is as follows:

The Dekatron displays of the timing and scaling units are both reset to zero, a clean planchette is in position ready to receive a new fraction, and a filled planchette, dried and ready for estimation, lies under the window of the Geiger counter. After 5 sec a pulse is passed from the timing unit to a thyratron, which fires and connects the output of the probe unit to the scaler, so that the scaler starts to count the activity of the dried sample. Simultaneously, the timing unit is reset to zero, and arrangements made to inhibit any further action at 5 sec.

Counting proceeds until the time set up on the first group of decade switches is reached, when a second thyratron is fired in the manner described above. This disconnects the scaler from the probe unit, breaks the coupling between the Dekatrons of the scaling unit to prevent any change in the display, and initiates the printing-out process. The filling and drying processes still continue until the second of the preset time intervals has elapsed, when another thyratron is fired. This energizes the turntable motor, which moves the table through one position, placing a clean planchette under the dropping tube and a new, freshly dried fraction under the counter. As the turntable completes its motion, a microswitch is operated to restore all circuits to their original condition and to apply reset pulses to both scaling and timing units, ready for the next cycle.

Experimental procedure

The chromatographic column is clamped in position over the second station of the turntable unit and the mixture under investigation is applied and washed in with a few drops of solvent. The solvent supply is then connected to the top of the column and the metering pump started. The supply magazine is filled with clean planchettes and trays and the storage magazine is emptied. The evaporation heaters are switched on and their controls set to the correct initial positions, which are determined if necessary by a previous experiment. The loading time control of the timing unit is set, with reference to the flow rate of the pump, to give the desired size of fraction and the counting time is also adjusted to the required value, which must of necessity be less than the loading time by at least

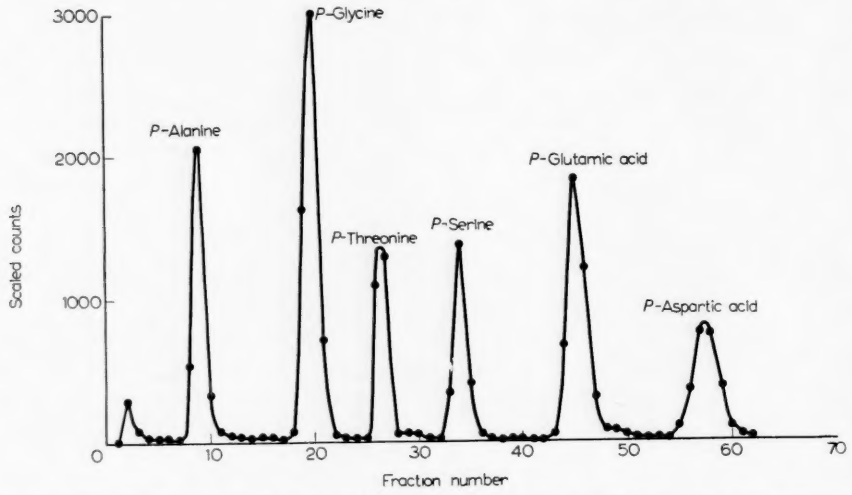

FIG. 8. Chromatogram of a mixture of I^{131} pipsylamino acids. Loading time: 320 sec. Counting time: 300 sec. Pumping rate: 6 ml/hr.

the 10 sec required for the operation of the recording unit. At the end of the chromatogram the timing unit is switched off and the column removed, and standards of known composition are put through the machine for the purpose of calibration.

The maximum load that can be applied to the column is determined by its dimensions and the nature of the chromatographic system, but in practice the load will be generally determined by the specific activities present in the mixture. With mixtures of substances of high specific activity it is better to limit the load so that the activity of no component is much greater than 10,000 counts/min to avoid large coincidence corrections due to the resolving time of the probe unit. On the other hand, when the specific activities of the components are low, the maximum load should be applied and, if necessary, the flow rate of the solvent reduced to allow sufficient time for accurate counting. With mixtures of several components of widely differing activities, a compromise is necessary in order to assess with accuracy those of low activity without exceeding 100,000 counts, the maximum number the scaling unit can indicate, in any fraction. This difficulty is peculiar to an automatic procedure, in which neither the counting time nor the geometry of the counting arrangement is varied during the course of a chromatogram, but it can be lessened by repeating the experiment under different conditions.

When a component is eluted from the column it is distributed over several fractions. If all the fractions are uniformly plated, the error involved in its radiometric determination depends on the amount of material present, the number of fractions required to collect it and the background count of the counter. In practice both the load and the size of the fractions are given the maximum values consistent with complete chromatographic separations of individual components and the limitations discussed above. The background count is minimized by housing the counter in a lead castle and by ensuring that the trays in the supply magazine are always scrupulously clean. Trays that have already been used are scoured with a suitable solvent and subsequently stored for a period equal to ten half-lives of the isotope before re-use. If long-lived isotopes have been employed, it is preferable to discard the trays altogether as new ones are cheap and simple to manufacture.

Calibration with standards of known composition is necessary to evaluate the results in terms of mass. Trays containing the dried deposits from known amounts of a suitable standard solution are prepared, either manually or in the machine, and are then counted like the other fractions. The recorded activities are used in the normal way to calculate the results.

Results

A mixture of the I^{131}-p-iodobenzenesulphonyl (pipsyl) derivatives of alanine, glycine, threonine, serine, glutamic acid and aspartic acid has been analysed and the result is shown graphically in Fig. 8. The apparatus previously described for gradient elution chromatography of this mixture[1] was modified by inserting the metering pump between

TABLE 1. Analysis of a mixture of I^{131}-labelled pipsylamino acids

Pipsyl (P) amino acids	Activity (counts)				Ratio (P-serine = 1·00)			
	1	2	3	4	1	2	3	4
P-alanine	948 × 10^2	299 × 10^2	336 × 10^2	300 × 10^2	1·54	1·42	1·40	1·41
P-glycine	1756	553	614	545	2·75	2·62	2·56	2·56
P-threonine	763	249	279	252	1·20	1·18	1·16	1·18
P-serine	637	211	240	213	1·00	1·00	1·00	1·00
P-glutamic acid	1273	416	460	421	2·00	1·97	1·92	1·97
P-aspartic acid	681	235	263	233	1·07	1·11	1·10	1·09

the saturator and the column proper. Table 1 shows the activities, corrected for coincidence losses, of the six components, obtained from four consecutive chromatograms. In the first experiment the weight of material applied to the column was *ca.* 0·03 mg and in the other three 0·01 mg. The ratios of the activities are also shown, taking the least, that of pipsyl–serine, as unity. The constancy of these ratios is an indication of the reproducibility of the machine when used for the assay of I^{131}, in virtually weightless samples.

The versatility of the machine is illustrated by the analysis of a mixture of amino acids from a protein hydrolysate. The mixture was partially separated by ion exchange chromatography using an acetate buffer (pH 4·0). The effluent was brought to pH 9·2 by the continuous addition of a phosphate–borax buffer containing the appropriate quantity of NaOH, and pumped through a small column of copper phosphate containing Cu^{64}. The effluent from this column, containing the labelled complexes of the amino acids, was passed to the machine. The samples produced for counting contained *ca.* 120 mg of inorganic salts, which appeared as a glass-like film over the bottom of the dishes. Fig. 9 shows the activities obtained, corrected for decay and coincidence losses, plotted against the fraction number. The activities of the six completely separated amino acids are shown in Table 2 and are compared with the optical densities obtained in a

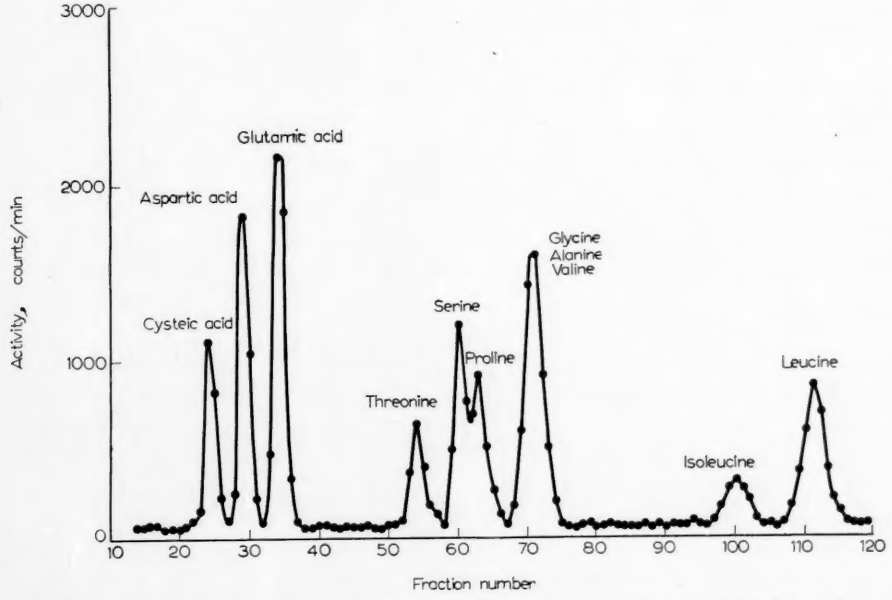

FIG. 9. Chromatogram of a mixture of amino acids estimated as the Cu^{64}-labelled copper complexes. Loading time: 720 sec. Counting time: 20 sec. Pumping rate: 13 ml/hr.

parallel experiment when the copper was estimated colorimetrically as the complex with sodium diethyl dithiocarbamate.

TABLE 2. Analysis of a mixture of Cu^{64}-labelled complexes of amino acids

Copper derivative of	Activity counts/min	Optical density	Ratio
Cysteic acid	2093	2·43	860
Aspartic acid	3120	3·50	892
Glutamic acid	5595	6·25	894
Threonine	1477	1·60	923
*Iso*leucine	999	1·09	917
Leucine	2996	3·45	868
			Mean 892

Discussion

The usual analytical procedure of counting "infinite thickness" samples of either the solid material or its solution results in low sensitivity per unit mass for all but the strongest β-emitters. The alternative procedure of counting the sample as a thin layer of material dried on a suitable support is often accompanied by considerable error arising from the unevenness of the plating. In the apparatus described here, automatic operation ensures that the plating procedure is exactly the same for all fractions. The dishes used are spherical in section, and when the heaters are correctly set the volume of liquid in the dish always remains small. The deposit is thus left as an even circular layer, about 1 cm diameter, in the centre of the dish and approximates to a point source from a radiometric standpoint. Highly reproducible results have been obtained for both "weightless" samples and those containing a considerable amount of solid. Plating on dishes of other shapes usually results in irregular annular deposits which cannot be positioned reproducibly under the counter.

The principle asset of chromatography, the achievement of quantitative separations of minute amounts of material, is exploited to the full in the machine by the use of small scale apparatus. This is possible because of the inherent sensitivity of the radiometric assay and because "carrier-free" preparations can be handled. In this connexion the use of an end window counter has considerable advantage over a liquid flow counter because of its greater sensitivity and ease of calibration.

The types of substances which can be investigated in the machine are limited because the end window counter employed cannot detect low energy α-particles and is very insensitive to γ-emitters. A greater flexibility would be achieved by using a scintillation counter but this expedient has not been adopted because most of the isotopes employed as tracers are β-emitters which can be detected very efficiently by means of the Geiger counter. The solvents employed for chromatography must be volatile at a temperature low enough to preclude thermal degradation of the material under investigation. If this is not so, the apparatus can be used without evaporation and the samples counted as liquids. In this case the size of the fraction is limited to the capacity of the sample tray, about 1 ml. In general, dry-counting is preferable because of its greater sensitivity and the absence of errors due to absorption of radiation by the solvent when gradient elution techniques are employed.

Acknowledgements—We wish to thank Dr. A. ROBSON for his continued interest in this work and much stimulating discussion. We are indebted to J. BROOKS for considerable help in the design of the turntable and recording units and to G. B. SHAW for their construction. Our thanks are also due to E. WEBSTER for assistance in the construction of the electronic equipment, and to A. AUSTIN for the illustrations.

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Automatic Electronic Inspection of Manufactured Systems Using Radioactive Components*

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An electronic system has been developed for the continuous inspection of small manufactured articles for the presence or absence of a vital part, in the case described the gas check ball of a certain type of ammunition primer. The critical part is tagged with a radioactive isotope, silver-110, and the assembled unit is passed on a conveyor belt under a scintillation detector. If the detector "sees" the part in question it operates a mechanical gate which deflects the inspected unit.

Some details are given of the electronic circuits, which employ transistors throughout, of the plating procedure used and radiation health considerations.

LE CONTRÔLE ÉLECTRONIQUE AUTOMATIQUE DES SYSTÈMES FABRIQUÉS AU MOYEN DE PIÈCES DÉTACHÉES

On décrit un système électronique pour l'inspection automatique de petits articles fabriqués auxquels peut manquer une partie essentielle, dans le cas, la petite sphère qui constitue la soupape à gaz dans des amorces de munitions. Les sphères sont rendues actives par placage à l'isotope d'argent Ag-110, et les amorces assemblées passent sur une courroie au-dessous d'un détecteur de scintillations. Si la partie active est décelée, un piston dévie sa course sur la courroie. Les circuits électroniques, transistorisés, sont décrits sommairement, et la méthode de placage des billes est décrite en detail, avec remarques sur les conditions sanitaires.

AUTOMATISCHE, ELEKTRONISCHE KONTROLLE VON TECHNISCHEN FABRIKATEN UNTER VERWENDUNG VON RADIOAKTIV MARKIERTEN TEILEN

Ein electronisches Gerät wird beschrieben, das gewisse fabrizierte Teile automatisch inspiziert um die korrekte Lage und die eventuelle Fehlung wichtiger Teilchen festzustellen, wie hier, z.B., das Rückstossgasventil eines Ammunitions primers. Der kritische Teil ist eine kleine Kupferkugel die mit der radioaktiven Isotope, Silber-110, markiert wird. Der komplete Primer wird dann auf einem endlosen Riemen unter einem Szintillationszähler vorbeibewegt. Wenn die Ventilkugel richtig da ist, aktuiert der Zähler eine mechanische Pforte, die den inspizierten Primer auf die andere Seite des Riemens verschiebt.

Einige Einzelheiten we den angegeben über die electrischen Stromkreise, welche Transistoren benutzen, den Plattierprozess and gesundheitliche Vorsichtsmassregeln.

* Published by permission of the Director, Mines Branch, Department of Mines and Technical Surveys, Ottawa and by agreement with Canadian Arsenals Ltd., Ottawa.

АВТОМАТИЧЕСКИЙ ЭЛЕКТРОННЫЙ КОНТРОЛЬ ИЗДЕЛИЙ С ПРИМЕНЕНИЕМ РАДИОАКТИВНЫХ КОМПОНЕНТОВ

Была разработана электронная система для непрерывного контроля наличия существенных деталей при изготовлении небольших изделий. Соответствующая часть изделия метится радиоактивным изотопом, серебром-110, после чего изделие в собранном виде помещается на ленту конвейера, проходящую под сцинтилляционным счетчиком. Если детектор ''видит'' меченую часть, то он приводит в действие механическое устройство, удаляющее изделие с ленты.

Приводятся некоторые особенности электронных цепей, в которых транзисторы применены по всей длине цепи, обсуждается методика покрытия, а также вопросы безопасности.

INTRODUCTION

THERE are many places in the industrial production of goods where a rigorous inspection of parts is necessary, but where purely visual inspection of an assembly is unsatisfactory owing to the inaccessibility of vital components. In such cases relatively complicated and expensive devices may be necessary to supplement mechanical gauges in order to assure the correct presence and position of an essential part. This applies particularly in the ammunition industry where the malfunction of an assembly may have particularly serious consequences and where more elaborate inspection procedures are mandatory. The equipment described in this article was developed specifically to establish the presence or absence of the copper ball gas check in a certain type of ammunition round, but the general principles of the method can be applied equally well to many other industrial inspection problems of that general nature.

The method involves the marking of the critical component with a radioactive isotope. After assembly the whole unit is then passed by a conveyor belt underneath a radiation detector which is actuated by the radiation from the component and operates a "kicker arm" or selector gate on the belt to direct the assembly into a chute for acceptable units. Absence of the active part means no action on the part of the kicker arm and arrival of the assembly at a chute for rejection. Similarly any failure of the detector system will lead to rejection of units so that the system fails safe. If desired, rejected units can be recirculated at a later time for rechecking.

DESIGN PRINCIPLES

Some previous experience had been available from work on automatic picker systems for radioactive ores.[1,2] In the present case the problem was greatly simplified by the constant shape and size of the units which made it possible to mount the detector quite close to the conveyor belt. The general function of the system is represented in the block diagram, Fig. 1.

The part to be checked in the ammunition primers was a small copper ball, called the gas check, which is placed in the primer between the cap and the fuse and acts as a valve to stop any backward gas flow when the round is fired. In an existing filling line it had been the practice to insert this gas check "peaball", about 3 mm in diameter, in the primer by hand, with a pierced disk then screwed on top of it. Inspection to confirm the presence of the gas check was carried out first by means of a pin probe and, at a later stage, by X-ray radiography, an expensive and time-consuming procedure.

Two methods were considered for radioactive marking of the peaball. The first involved irradiating all the balls in a nuclear reactor and was rejected as impractical, both because of the short half-life of copper-64 and because of the expense and transportation problems involved in shipping the

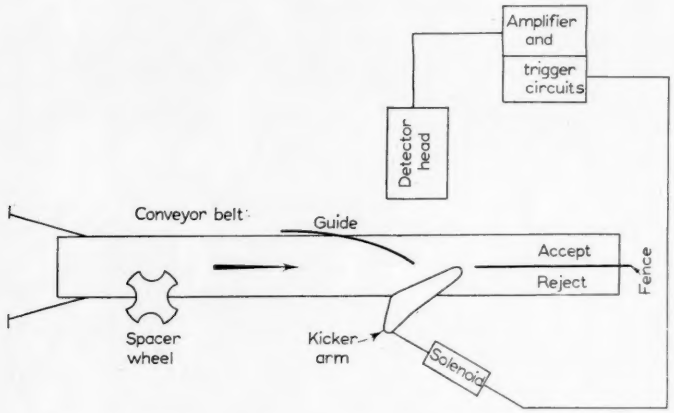

FIG. 1. Block diagram of inspection system.

balls from the plant to Chalk River and back again. Instead it was decided to deposit the activity on the surface of the balls by plating and then to detect the active balls by means of a scintillator detector for high sensitivity.

CHOICE OF ISOTOPE AND LEVEL OF ACTIVITY

The choice of isotope was governed by several factors: the activity had to be sufficiently long-lived to permit storage of the active balls for one or two months, the element in question had to have properties to make deposition on the balls easy and permanent, it had to be non-corrosive and acceptable to Inspection Service authorities. Silver-110 was the isotope selected as meeting these requirements. It emits both energetic beta and gamma rays, making it easy to detect. Preliminary experiments showed that a satisfactory method of tagging could be developed by bathing the balls in a silver cyanide solution containing a small amount of the radioactive isotope. Silver-110 has a half life of 270 days so that the balls can be stored for several months after plating, if necessary, without losing too much of their activity. As the detector could be arranged very close to the primers on the belt a low level of activity per ball was sufficient to actuate the sorting mechanism.

After several tests with varying amounts of Ag-110, it was found that as little as 0·05 μc was enough for positive identification. However, there is a small variation in the amount of silver that the check balls will take, and a safety correction had to be applied. An added correction was also required to compensate for possible fluctuations of the detector sensitivity. Finally, another margin of safety should take care of the decay of the silver between the time at which the balls are plated and the time at which they are actually tested. It was therefore decided to use between 0·25 and 0·30 μc per ball.

PLATING PROCEDURE

The peaballs are first degreased by agitation in a 5% solution of KOH. After thorough washing, they are pickled for one minute in a 5% solution of sulphuric acid. They are then washed free from acid, and plated as soon as possible, without undue exposure to the atmosphere. A pickled surface oxidizes very rapidly.

All the operations are performed in a special plastic container. Four vanes fixed to the wall of the container ensure thorough agitation. A Saran screen sealed at one extremity allows easy washing without fear of losing any balls. In use the container is placed on rollers and rotated during the plating operation.

The composition of the plating bath was suggested by the Dominion Arsenal Division of Canadian Arsenals Ltd. and is as follows:

Reagents required for plating bath:

2·5 g	$AgNO_3$
12·5 g	KCN
12·5 g	Na_2CO_3
5·0 g	NaCl
20 ml	NH_4OH

A solution is prepared by dissolving the KCN, Na_2CO_3, NaCl and NH_4OH in 1 litre of water.

The required amount of radioactive silver is weighed, and dissolved in a minimum amount of nitric acid. The radioactive silver nitrate is washed into a beaker with the 2·5 g of natural silver nitrate and the silver chloride is precipitated from the hot nitrate solution, using an excess of sodium chloride. The precipitate is filtered on a Gooch crucible, and washed. After washing, the *fresh* precipitate is dissolved in the cyanide solution by simply placing the Gooch crucible in the solution and bringing to the boiling point.

As the plating reaction is one of chemical replacement, there is a limit to the amount of total silver that will plate on the peaballs, at a given temperature and for given pickling conditions. The effect of pickling is especially important. Repeated pickling and exposure to air or aerated water will increase the effective area of a piece of copper, and the quantity of silver that will plate will increase correspondingly.

For that reason, it was decided to use a bath containing much less than the required amount of silver for maximum plating. In this way all the silver in the solution is plated out, the activity of the peaballs is accurately known, and there is no problem of recovery or disposal of radioactivity in the spent solutions. The amount of silver in a one-litre standard bath (2·5 g) is sufficient to plate 10,000 peaballs with about 0·2 mg Ag per ball, which is about one-tenth of the maximum possible amount with the type of pickling used. The use of this bath formula thus ensures quantitative removal of the silver from the bath.

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DESCRIPTION OF THE EQUIPMENT

Preliminary experiments with a modified ore picker were carried out at the Mines Branch, Ottawa, to establish the feasibility of the method. When it was clear that the necessary sensitivity could be obtained with a low level of activity, a unit was constructed to meet the requirements of the Filling Division of Canadian Arsenals Ltd. These included precautions to make the units and the wiring explosion-proof.

The conveyor belt and mechanical lay-out were designed by the Filling Division of Canadian Arsenals Limited. The electronic system was designed and built at the Radioactivity Division of the Department of Mines and Technical Surveys in Ottawa. Only the main features will be described here as details have appeared elsewhere.[3] As the system had to operate for long periods with a minimum of maintenance it was decided to transistorize the system as far as seemed feasible. This reduced the working voltages and hence explosion hazards, and made a need for component replacement less likely. The only major problem was the cooling of the last power transistor which was arranged by connection to the compressed air line so that a steady flow of cool air was blown through the main electronic unit. Since there are few practical circuits of this nature in the literature, the circuit diagrams are presented in Figs. 2 and 3 and are largely self-explanatory.

The detector head consists of a $1\frac{1}{2}$ in. diameter, $1\frac{1}{2}$ in. long, thallium-activated sodium iodide crystal, mounted dry in a

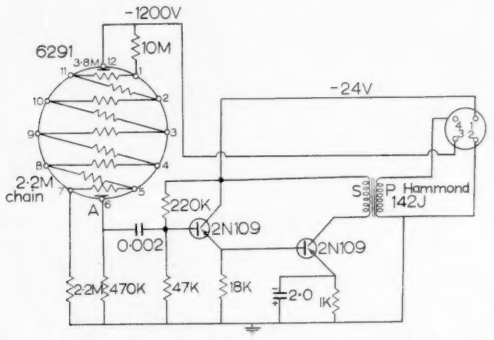

FIG. 2. Detector head for the primer inspection unit.

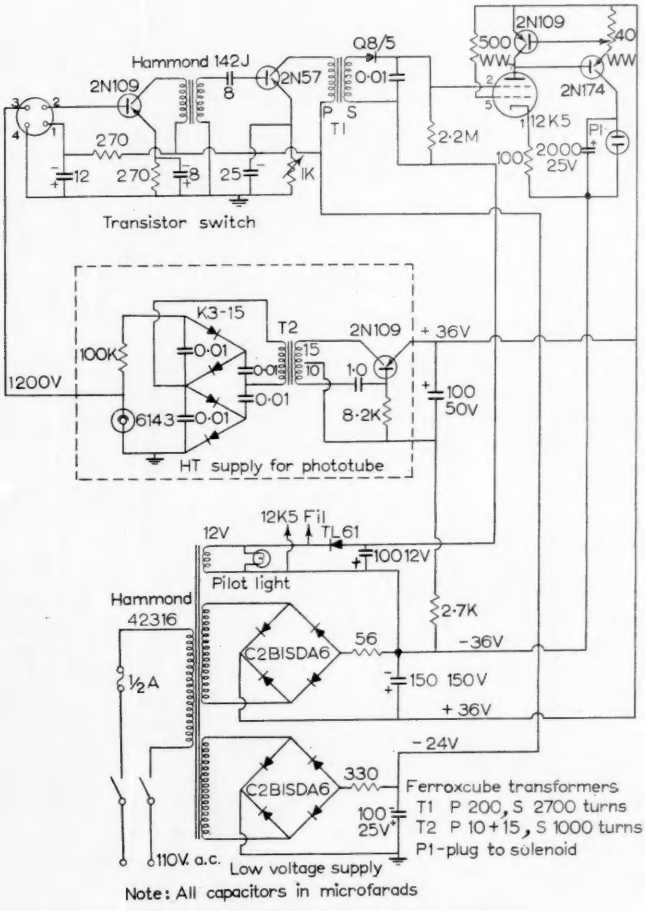

FIG. 3. Circuit of primer inspection unit.

special holder, and placed under the photocathode of a Dumont, type 6292 photomultiplier tube. Its electronic circuit is shown in Fig. 2. The output from the pre-amplifier in the detector head is fed by coaxial cable to the main electronic unit whose circuit is shown in Fig. 3. It consists of an amplifier and trigger system and a high and low voltage power supply. These are all mounted on the same chassis and enclosed in a large box. Further details of operation of the circuit are given in reference 3. The conveyor belt was made from 1/32 in. fabric strip, 1½ in. wide, and was driven by a chain drive from an enclosed motor at a speed of 15 ft/min. The spacer shaft was geared to the belt drive. Various spacings can be obtained by using different spacer disks. A microswitch was installed later in a position just ahead of the detector as a safeguard. Every primer passing this switch would momentarily break the solenoid circuit and thus ensure its readiness for the arriving primer.

RADIATION HEALTH CONSIDERATIONS

One of the main factors of interest to prospective users is the problem of radiation exposure and possible hazards associated with it. The highest level of activity is that associated with the plating solution; each subsequent stage represents a dilution step and hence lower radiation level. Exposure during the plating can be kept down by shielding and careful handling as described above. At the Filling Plant the highest concentration was encountered at the hopper used for loading the primers. A funnel filled with 2000 peaballs was surrounded by ¼ in. lead sheet and it was found that the activity on the outside was less than one tenth of the maximum permissible. For routine work a special heavy lead hopper was designed. The exposure to the operator was quite negligible at all times.

The radiation levels at all subsequent stages of the operation were monitored in co-operation with a representative of the Department of National Health and Welfare. The dosage level to any operator was found to be negligible and the count-rate from assembled primers and groups of packaged rounds was not detectable. It can, therefore, be stated definitely that the use of the procedure described in this paper results in no radiation hazard to any operator or user.

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CONCLUSIONS

The system described above has been tested in normal filling operations and appears to work satisfactorily. It is easy to run and to maintain, and little trouble is anticipated on this score as long as care is taken to cool the trigger unit with compressed air. In future models a few minor circuit changes may be incorporated, particularly to improve temperature stability.

Similar inspection systems could be adapted for a variety of applications in this field and it is hoped that this work will prove of wider usefulness. In particular for short term inspection processes, shorter-lived isotopes could be used to advantage.

Acknowledgements—The work was done in co-operation with the Filling Division and Dominion Arsenal Division of Canadian Arsenals Limited. It is a pleasure to acknowledge the assistance of Mr. A. H. Bettens, of the Mines Branch, Ottawa, in the construction and lay-out of the electronic units.

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Radiolysis of Normal Heptane and its Inhibition by Dibenzyl Sulfide and Dibenzyl Additions

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Kinetic investigations of normal heptane γ-radiolysis were carried out over a wide dose range. The composition of gases from radiolysis was studied in detail. The inhibiting effect of small additions (5×10^{-4} M) of dibenzyl and dibenzyl sulfide was determined. A decrease in the amount of unsaturated gases and the appearance of isomeric structures with increase of the integral dose rate was observed.

LA RADIOLYSE DU NORMAL-HEPTANE ET SON INHIBITION PAR DES SUPPLÉMENTS DE SULFURE DE DIBENZYL ET DE DIBENZYL

Des recherches kinétiques furent achevées sur la radiolyse γ du normal-heptane à travers grande rangée de doses. La composition des gaz produits par la radiolyse fut précisée. L'effet inhibitif de petits suppléments (5×10^{-4} M) de dibenzyl et de sulfure de dibenzyl fut déterminé. On observa une diminution de la quantité de gaz non-saturés et l'apparence de structures isomériques avec augmentation du taux de la dose intégrale.

РАДИОЛИЗ НОРМАЛЬНОГО ГЕПТАНА И ЕГО ИНГИБИРОВАНИЕ ДОБАВКАМИ ДИБЕНЗИЛСУЛЬФИДА И ДИБЕНЗИЛА

Исследована кинетика γ-радиолиза нормального гептана в широком интервале доз. Детально изучен состав газов радиолиза. Определено ингибрующее влияние малых добавок ($5 \cdot 10^{-4}$ M) дибензила и дибензилсульфида. Отмечено уменьшение содержания непредельных газов и появление изомерных структур с увеличением интегральных доз.

RADIOLYSE VON NORMALHEPTAN UND IHRE HEMMUNG BEI ZUSATZ VON DIBENZYL UND DIBENZYLSULFID

Kinetische Untersuchungen über γ-Radiolyse van Normalheptan für einen weiteren Dosisbereich wurden durchgeführt. Die Zusammensetzung der aus der Radiolyse stammenden Gase wurden eingehend untersucht. Es wurde der Hemmungseffekt bestimmt bei kleinen Zusätzen (5×10^{-4} M) von Dibenzyl und Dibenzylsulfid. Mit Zunahme der Integraldosisrate wurde eine Abnahme der Menge der gesättigten Gase und ein Auftauchen isomerer Strukturen beobachtet.

γ-RADIOLYSIS of normal heptane in the liquid phase, and of dibenzyl sulfide and dibenzyl solutions in heptane was investigated. The main objects of this work were: (i) proper determination of radiolysis kinetics at the initial stages and, in particular, of the effect of interruption in irradiation; (ii) detailed evaluation of the gas constituents and yield over a wide dose range (exceeding three orders of magnitude); (iii) determination of the relative effectivity of the inhibiting effect of dibenzyl sulfide and

dibenzyl additions.* Apart from its general importance such an investigation was brought about by the necessity of determining the effect of sulfur compounds in radiolysis of oil products.

The sources used were: (a) for small doses: an X-ray apparatus of the Russian mark RUP-3 working at a tension of 300 kV, a tube current of 5 mA, and a focal current of 0·75 A. The tube used was of the Russian mark BPV-400 with an annular radiation output via a withdrawn grounded anode. The dose rate in the irradiation cell was determined by a ferrous sulfate dosimeter and found to be 3×10^{15} eV/cm^3 per sec; (b) a Co^{60} source with a nominal activity of 20 kilocurie was used for high doses.

The following technique was used for studying the kinetics of radiolysis at low doses. The ring irradiation cell made from Pyrex was located in the near vicinity of the tube anode. The upper part of the cell was connected with a membrane manometer via a short connecting tube. The readings of the manometer were taken by a recording electronic potentiometer of the Russian mark EPP-09† by means of a differential photoelement. The sensitivity of pressure measurements was 5×10^{-2} mm Hg per 1 mm of the potentiometer tape. Irradiation was carried out in two cells. The volumes of liquids contained in the cells were 30 and 8 ml respectively. A temperature of $9 \pm 0{\cdot}05$°C was maintained throughout the experiment by means of an ultrathermostat. The temperature control was automatic. On Co^{60} exposure the irradiated product was contained in special zirconium glass ampoules.

Commercial heptane was purified to practically complete transparency in ultraviolet light. Possible impurities consisting of higher and lower paraffins were not detected mass-spectrometrically. Dibenzyl sulfide was synthetized by the usual procedure, repeatedly recrystallized, and its constant values and spectrum in the ultraviolet region were found to correspond to tabular data. Dissolved air was removed from all samples before irradiation by repeated freezing and pumping off by a diffusion pump. Gas analysis was carried out by means of the gas–liquid partition chromatography technique, essentially similar to that used in refs. 2 and 3. This method permits analysis of 0·5 cm^3 gas samples (up to C_5 incl.) to be carried out with a relative precision of 2–5 per cent for each constituent, and with a high degree of sensitivity. It will be noted that the technique used should be elaborated with special care, as even slight discrepancies in method would lead to inadequate results in gas analyses.[4,5]

Therefore the technique of analysis will be considered here in detail. The gaseous products were always divided into two fractions: the first contained methane and hydrogen, and the second C_2 and higher substances. Almost all authors obtained the first fraction by the same method, which consisted in extracting the fraction from hydrocarbon frozen in liquid nitrogen, by adsorption on coal. There is nothing to be said against it. But mass-spectrometric analysis as used in ref. 5 seems to be less adequate. At low methane content of hydrogen the former cannot be detected with the required precision, since the peaks for residual air become commensurable with those for methane. Thus adsorptional separation of methane and hydrogen on activated coal appears to be preferable, maximum precision being obtained by carrying out the analysis *in vacuo* and measuring the pressure with a membrane manometer, as has been done in this work. Isolation of the second gaseous fraction (C_2–C_5) from liquid hydrocarbons involves certain difficulties due to solubility and to small difference in vapour tensions of various hydrocarbons. As has been shown by special experiments, the technique used in the works mentioned permitted one to obtain from heptane, for instance, not more than 70, 50 and 10 per cent of the fractions

* All subsequent data refer to dibenzyl sulfide and dibenzyl solutions having a concentration of 5×10^{-4} M.

† The recording scheme used by the authors is a modification of the Kosourov method.[1]

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C_3, C_4 and C_5 respectively. The solution of this problem was based on the fact that at $-80°$ the vapour tension of the gases remaining over heptane after isolation of the first fraction was practically zero. A sample of heptane together with the dissolved gases was collected into a special ampoule at $-80°$. The ampoule was introduced into the apparatus and broken there. Heptane and the gases it contained were analysed. Analysis was made by means of gas–liquid partition chromatography, di-*iso*-amylphthalate and acetonyl-acetone being used as the impregnating liquid. The overall length of the column was 15 m. Not only hydrocarbons but even small hydrogen sulfide additions could be detected by this method.

At low dose rates the yields were directly proportional to the time of irradiation. If irradiation was interrupted, the liberation of gases stopped immediately. On resumption of irradiation the straight line corresponding to the gas yield was in fact continuing the initial line (Fig. 1). Thus it can be stated

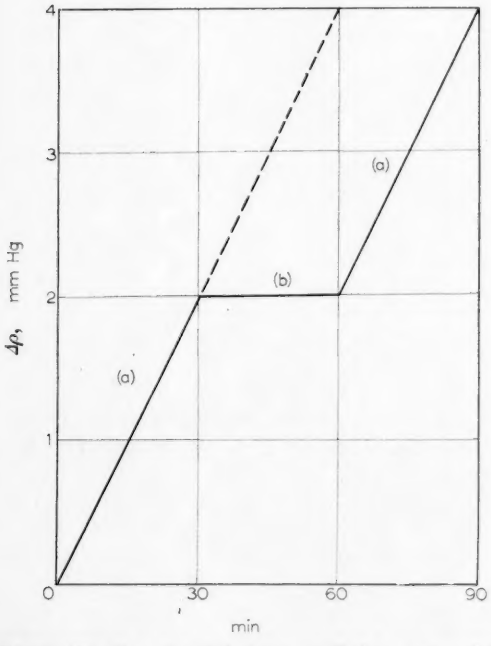

FIG. 1. Kinetics of radiolysis at small dose rates: (a) constant irradiation, (b) intermittent irradiation.

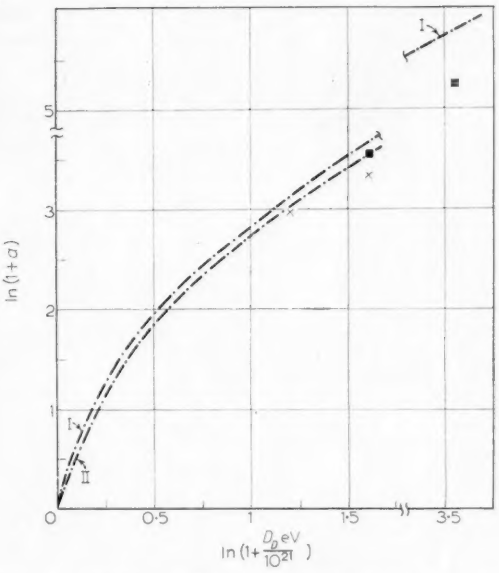

FIG. 2. Kinetics of hydrogen and methane liberation in radiolysis. Continuous curves at the origin of the co-ordinates describe experimental evidence obtained at low dose rates. Broken-dotted lines correspond to the linearity of gas liberation. I and rectangles designate pure heptane, II and crosses the dibenzyl sulfide solution in heptane.

with a very high degree of accuracy that no radiation "hysteresis" was observed. Direct gas measurements carried out by this method have shown that the amount of hydrogen and methane dissolved in heptane is not considerable, the Henri law being obeyed. Fig. 2 shows the hydrogen and methane yields at a function of the dose rate for pure heptane and for a dibenzyl sulfide solution. To express by one plot all the evidence obtained over a wide integral dose range

$\ln (1 + a)$ and $\ln (1 + \frac{D_D \text{ eV}}{10^{21}})$ are plotted

along the axes of abscissae and ordinates respectively, retaining the aspect of the curve in usual co-ordinates at low degrees of radiolysis. Here a designates the methane and hydrogen yields in cm^3 per 10 ml of substance, and D_D the dose rate as measured by a ferrous sulfate dosimeter. Deviations from the linearity, which is expressed in Fig. 2 by the broken-dotted

line, begin with integral doses of the order of $D_D = 10^{21}$ eV/ml. The inhibiting action of dibenzyl sulfide with respect to heptane radiolysis can be distinctly seen from Fig. 2. In the linear zone the hydrogen–methane yield decreases by approximately 15 per cent.

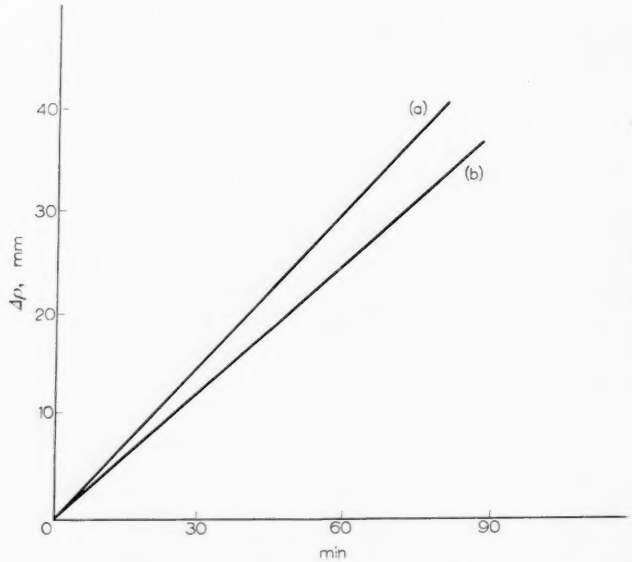

FIG. 3. Kinetics of heptane radiolysis (a) and protective effect of dibenzyl sulfide and dibenzyl additions (b) at small dose rates.

Fig. 3 shows the initial course of radiolysis for pure heptane (a) and dibenzyl sulfide and dibenzyl solutions (b). It will be emphasized that the protective effect of equal dibenzyl sulfide and dibenzyl additions is practically the same.

To determine the absolute values of radiation-induced yields (G) the dose rates as measured by a ferrous sulfate dosimeter were recalculated to the *n*-heptane dose rate, taking into account that the absorption is directly proportional to the density and effective atomic number of the heptane related to those of the dosimetry system. Thus the heptane dose rate

$$D_{C_7H_{16}} = D_D \frac{\rho C_7H_{16} \times \bar{Z}_{C_7H_{16}}}{\rho_D \times Z_D}$$

where $\bar{Z} = \sqrt[2.94]{\frac{\Sigma n Z^{3.94}}{\Sigma n Z}}$, and ρ_i are densities (see, for instance, ref. 6). Since non-linear effects were shown to occur already at a dose of 10^{21} eV/ml, and at lower doses only measurements of hydrogen and methane yields appeared to be possible, the G values are given only for these gases: $G(H_2) = 4{\cdot}9$; $G(CH_4) = 0{\cdot}22$. The value of $G(H_2) = 4{\cdot}9$ is fairly near to that given in ref. 4 $-G(H_2) = 4{\cdot}7$. It will be noted that the methane yield $G(CH_4) = 0{\cdot}09$ reported in ref. 4, and also the linear dependence of the yield upon the dose[4,5] are not consistent with our results,* as can be seen from the evidence for pure heptane (Table 1).

The C_2–C_5 gas fraction for pure heptane at an integral dose of $D_D = 3{\cdot}25 \times 10^{22}$ eV/ml amounts to 20·5 molar per cent of the total yield.

The results of gas analysis are given in Table 2 (in molar per cent).

The following conclusions can be drawn

* Deviations from the linear law were observed both for hydrogen and methane, being more pronounced in the case of the latter. This is apparently accounted for by the already mentioned inadequacy of the mass-spectroscopic method for detecting small amounts of methane.[5] All the analyses made by DEWHURST are in fact related to the non-linear region.

TABLE 1

D_D eV/ml	Fraction I yield cm³ per 10 ml of substance	Composition of the fraction	
		H_2 molar per cent	CH_4 molar per cent
$1{\cdot}6 \times 10^{19}$	0·15	no analysis was made	
$3{\cdot}2 \times 10^{19}$	0·30	95·9	4·1
4×10^{21}	34	96·6	3·4
$3{\cdot}25 \times 10^{22}$	193	98	2

from the evidence obtained:

1. Non-linear effects become apparent beginning with integral doses of $D_D = 10^{21}$ eV/ml and are observed for all constituents. For methane for instance the non-linearity can be readily explained by the interaction of CH_3 radicals with products from the radiolysis. This is in agreement with general conceptions of the course of the process.

2. The scission of the C–C bonds, both with production of alkyl radicals and with direct formation of the end-products, saturated and unsaturated, plays a very important part in alkane radiolysis. This stage of the latter is somewhat similar to thermal cracking of hydrocarbons with a thermal shock that is short in time, but very intensive.

3. It will be noted that acetylene was found among gases from the radiolysis (it seems to be the first time that it was observed in alkane radiolysis). Its relative amount decreases with increase of the integral dose. The concentration of other lower olefines also decreases in the course of the radiolysis, showing the important effect of secondary reactions of lower olefines. In general radiolysis reduces the hydrogen content in the liquid phase.

4. The diversity of gases from the radiolysis and the relatively high abundance of isomeric structures, probably of secondary origin, is of great importance. The full composition of gases from the radiolysis seems to be reported for the first time.

5. No hydrogen sulfide was found among the gases from radiolysis of the dibenzyl sulfide solution in heptane. It means that

TABLE 2. Composition of gases from the radiolysis

Constituents	D_D eV/ml				
	n-Heptane		Dibenzyl sulfide solution in heptane		
	$3{\cdot}2 \times 10^{19}$*	4×10^{21}*	$3{\cdot}25 \times 10^{22}$	$2{\cdot}4 \times 10^{21}$	4×10^{21}
Hydrogen	95·9	96·6	79·5	70·1	73·27
Methane	4·1	3·4	1·6	2·37	1·54
Ethane		97·2	3·2	6·46	8·03
Ethylene			0·22	2·30	
Acetylene		2·8	0·02	4·37	0·09
Propane			4·57	3·30	5·27
Propylene			0·32	1·41	0·85
n-Butane			4·49	3·98	3·31
i-Butane			0·09	—	—
i-Butene + Butene-1			0·18	1·53	1·36
n-Butene-2			0·26	—	—
i-Pentane + 3-methylbutene-1			0·22	—	—
n-Pentane			4·83	4·18	6·29
2-methylbutene-1			0·3	—	—
2-methylbutene-2			0·2	—	—
Hydrogen sulfide			—	—	—
The total gas yield cm³ per 10 ml of liquid			234·5	24·9	36·6

* Content for separate fractions. No other analyses were made in these experiments.

in the cases considered the decomposition of dibenzyl sulfide with liberation of hydrogen sulfide did not exceed 10 per cent of its total amount. The protective effect in this case is presumably based on excitation transfer.

6. The small effect of the sulfur atom is confirmed experimentally by the protective effect of dibenzyl sulfide and dibenzyl additions. It is apparently due to screening of the sulfur atom by the aromatic nuclei.

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Chambre d'Ionisation β–γ

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Description d'une chambre d'ionisation destinée au contrôle de l'activité de solutions ou de sources radioactives au stade d'utilisation. Cette chambre est plus particulièrement prévue, en raison de sa gamme de sensibilité et de ses possibilités pour usages médicaux.

Trois types de mesures sont possibles:

(1) Mesure de l'activité spécifique de solutions émettrices β, à partir de 50 μc/cm^3.
(2) Mesure de l'activité de sources solides ou liquides γ, à partir de 1 mc.
(3) Contrôle de la dose à la surface d'applicateurs β utilisés en bétathérapie.

La chambre peut servir d'étalon secondaire, si l'expérimentateur a effectué les étalonnages nécessaires.

β–γ IONISATION CHAMBER

This chamber is designed for activity control of radioactive solutions at the time of utilization. In consideration of its sensitivity scale, this chamber is especially convenient for medical purposes.

Three types of measurement are possible:

(1) Measurement of specific activity of β-emitter solutions above 50 μc/cm^3.
(2) Measurement of γ-emitters—solid or liquid—above 1 mc.
(3) Dose control at the surface of β-applicators used in betatherapy.

This chamber can be used as a standard after calibrating with standard solutions.

ИОНИЗАЦИОННАЯ КАМЕРА ДЛЯ ИЗМЕРЕНИЯ β И γ ИЗЛУЧЕНИЙ

Данная камера предназначена для контроля активности радиоактивных растворов во время их применения. Шкала чувствительности этой камеры делает ее особенно пригодной для медицинских целей.

Возможны три типа измерений: измерение удельной активности растворов β-излучателей с активностью выше 50 μc см^3, измерение γ-излучателей, твердых или жидких, активностью выше I Mk и дозиметрия на поверхности β-излучателей, применяющихся в бетатерапии.

После калибровки камеры стандартными растворами она может быть использована как эталонная.

EINE β–γ-IONISATIONSKAMMER

Diese Kammer wurde zum Zwecke der Aktivitätskontrolle für radioaktive Lösungen unmittelbar bevor diese zur Verwendung gelangen entworfen. Der Empfindlichkeitsbereich wurde so gewählt, dass die Kammer besonders für medizinische Zwecke geeignet ist.

3 Arten von Messungen sind möglich:

1. Messung der spezifischen Aktivität von β-strahlenden Lösungen von über 50 μc/cm^3.
2. Messung von γ-Strahlern in flüssiger oder fester Form über 1 mc.
3. Dosiskontrolle an der Oberfläche von β-Applikatoren welche für β-Therapie verwendet werden.

Wenn die Kammer mit Hilfe von Standardlösungen geeicht wurde, kann sie zur Kalibrierung benützt werden.

BUT DE L'APPAREIL

Cette chambre est destinée au contrôle de l'activité de solutions ou de sources radioactives au stade utilisation.

Elle doit permettre aux laboratoires non spécialisés en mesures absolues de déterminer avec une précision raisonnable l'activité des solutions qu'ils utilisent. En particulier, sa gamme de sensibilité doit en faire un instrument commode pour la mesure de l'activité des solutions utilisées dans les hôpitaux.

Pour les β, cet appareil convient aux activités supérieures à 50 $\mu c/cm^3$ environ. Pour les γ, le seuil se situe aux environs de 1 mc. Dans ces domaines d'activité, le compteur G.M. serait d'un emploi malaisé (dilutions nécessaires, corrections de pertes de comptage, etc . . .).

Enfin, cette chambre peut permettre d'effectuer des mesures sur les applicateurs utilisés en bétathérapie.

DESCRIPTION DE L'ENSEMBLE

La partie essentielle de la chambre consiste en trois électrodes planes parallèles, l'électrode collectrice étant située entre deux électrodes haute tension. Toutes trois sont des feuilles d'aluminium de 1,3 mg/cm².

Cet ensemble est enfermé dans un cylindre d'aluminium dont les faces supérieure et inférieure sont percées d'un trou central qui peut être obturé par des diaphragmes de différents diamètres.

Le préamplificateur associé est situé sous la partie sensible de la chambre, et il est lui-même connecté à un amplificateur à courant continu. La résistance d'entrée est de 10^{11} ohms. Un coffret d'accessoires contient une source étalon, des porte-sources, des coupelles et un jeu de diaphragmes.

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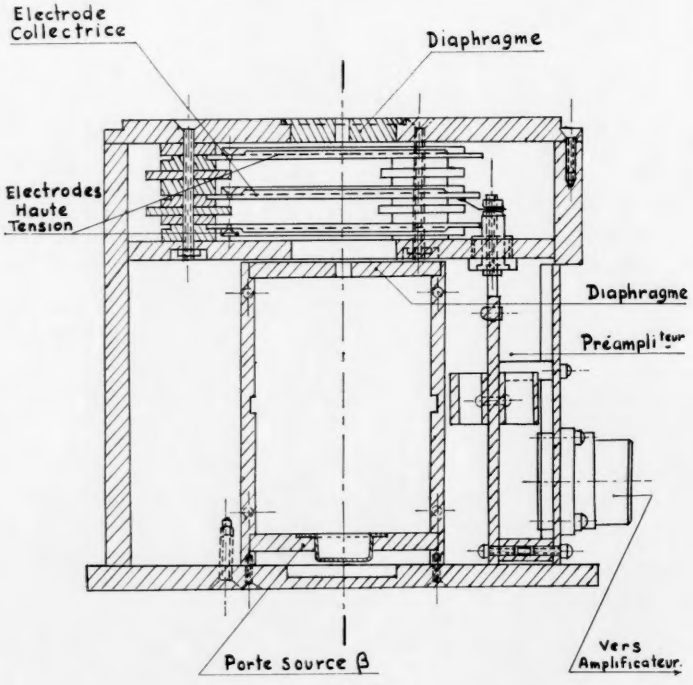

Fig. 1.

MESURE DE L'ACTIVITE SPECIFIQUE DE SOLUTIONS D'EMETTEURS β

On verse 1 cm³ de la solution dans une des coupelles. Leur diamètre est tel que la hauteur de liquide soit plus grande que le parcours dans l'eau des β de 1 MeV. Dans ces conditions, une erreur de pipetage même de 10 pour cent n'aura qu'une influence négligeable sur la mesure.

La coupelle est placée sur son porte-source en une des positions 1 ou 2 suivant l'activité (Fig. 2).

Ces positions ayant été étalonnées pour divers radioéléments, de la tension lue pour l'échantillon considéré, on déduit l'activité spécifique de la solution.

Par exemple, en position 2, l'étalonnage pour le P^{32} est de 1,72 V par mc/cm³.

Les chambres d'ionisation ne pouvant être rigoureusement identiques entre elles, il est préférable que chaque utilisateur étalonne sa chambre à l'aide de solutions étalon de radioéléments qui l'intéressent. Ces solutions étalon sont délivrées par les laboratoires spécialisés en mesures absolues.

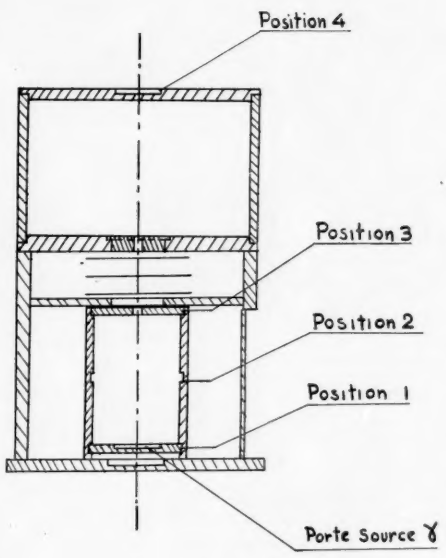

FIG. 2.

MESURE D'EMETTEURS γ

On place l'échantillon sur le porte-source γ d'abord en position 1, puis en position 4. On note la tension lue pour ces deux positions. La tension de mesure est la moyenne entre ces deux valeurs de tension.

Ces mesures couplées permettent d'éliminer le facteur géométrique de la source: l'étalonnage pour une source ponctuelle sera encore valable pour une source de dimensions finies (à condition que l'autoabsorption ne soit pas trop importante). En particulier, on pourra contrôler ainsi les flacons contenant les solutions radioactives si celles-ci sont émettrices γ.

En effet, chacune de ces positions est à une distance de 10 cm de l'électrode collectrice. Si une partie de la source est plus proche de l'électrode collectrice en position 1, elle s'en trouvera plus éloignée un position 4. Dans ces conditions, en prenant la moyenne des deux mesures, on a compensation au premier ordre près de l'erreur sur les courants (Fig. 2).

La formule reliant l'activité de l'échantillon cherchée A exprimée en millicuries à la tension de mesure V volts est simplement:

$$A = 100 \frac{V}{K}$$

où K est le coefficient caractéristique du radioélément considéré (dose en roentgens par heure donnée par une source de 1 mc à 1 cm).

Le coefficient 100 résulte des dimensions adoptées pour la chambre, de la nature de ses parois et de la géométrie de l'ensemble source-chambre.

En réalité, cette formule n'est pas rigoureusement exacte, car elle suppose que la chambre remplit les conditions de Bragg-Gray, ce qui n'est pas le cas pour toutes les énergies.

Expérimentalement, on trouve qu'elle n'est valable qu'à partir de 0,5 MeV. Pour les énergies inférieures, il sera nécessaire de procéder à un étalonnage préalable.

CONTROLE DES APPLICATEURS RADIOACTIFS MEDICAUX

Ces applicateurs, utilisés en bétathérapie externe sont constitués en général d'une feuille de matière plastique contenant un radioélément incorporé.

Pour ce type de mesure, on enlève le manchon amovible et on place l'applicateur au contact de la face plane supérieure de la chambre.

(a) *Contrôle d'homogénéité*

En faisant défiler l'applicateur sur un des diaphragmes supérieurs, et en notant la tension en fonction de sa position, on peut tracer la carte l'activité de l'applicateur.

(b) *Evaluation de la dose à la surface*

En mesurant dans cette géométrie un émetteur β étalonné en couche épaisse (par exemple une solution de P^{32}) pour lequel la dose à la surface est calculable, on peut établir une échelle de correspondance pour étalonner en rad/h l'indication de l'appareil. Cet étalonnage permet ensuite de mesurer la dose à la surface d'un applicateur pour lequel les conditions de couche épaisse ne sont plus réalisées.

La dose–profondeur peut être mesurée en interposant entre applicateur et chambre des écrans tissu équivalents.[1]

SOURCE ETALON

Cette source permet de tenir compte de l'influence des conditions atmosphériques sur les indications de l'appareil et de contrôler le bon fonctionnement de celui-ci.

Le rapport des tensions lues pour l'étalon dans les conditions normales de température et pression et dans les conditions ambiantes donne le coefficient de correction à appliquer pour la mesure d'un échantillon.

Cette source étalon d'une centaine de microcuries de Sr^{90}-Y^{90} a été complétée par un écran de plomb de 4 mm d'épaisseur qui, lorsque la source est sortie de la chambre, vient automatiquement occulter le faisceau de rayonnement émis par la source, évitant ainsi les risques d'irradiation de l'opérateur.

CONCLUSION

La chambre décrite permet des mesures rapides d'émetteurs β et γ. Son utilisation dépend de l'expérimentateur: elle peut servir soit de détecteur destiné à des mesures relatives, soit d'appareil étalon secondaire si l'expérimentateur a effectué les étalonnages nécessaires.

L'activité des solutions étalon étant en général connue à ± 3 pour cent près, la linéarité et la fidélité de la chambre étant meilleures que ± 2 pour cent, la chambre permettra alors d'opérer des mesures à ± 5 pour cent près.

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technical notes

Nitrogen Fixation by the Action of Ionizing Radiations*

(*Received* 16 *June* 1958)

CONTEMPORARY developments in nuclear engineering raise the question of developing suitable methods of using the power released in nuclear reactions. The direct oxidation of nitrogen by the action of radiations and high energy particles might be visualized as one of these methods.

The present investigation is concerned with the study of the main rules governing the oxidation of nitrogen arising from the effect of electron collisions and of γ-rays. A 2 kV electron-beam tube, a 200 kV linear accelerator and a 1400 c Co^{60} artificial source were used to produce the radiation.

Measurements were made of the rate of formation of nitrogen oxides as a function of the duration of the irradiation, the composition of the gaseous mixture, the pressure, and the temperature, and led to the following equation for the reaction rate:

$$V = KP_{N_2} \cdot P_{O_2} \qquad (1)$$

where V is the reaction rate, K a constant, $\sim P_{N_2}$ and P_{O_2} the nitrogen and oxygen partial pressures.

Equation (1) holds good for pressures of ~0·1 and ~760 mm Hg.

The activation energy of the reaction is 7·5 ± 1 kcal/mole at low pressures and about 2 kcal/mole at atmospheric pressure.

As has been established[1,2] the reaction begins at an electron energy of 16·2 eV which corresponds to the potential at which molecular nitrogen ions N_2^+ appear. An appreciable increase of the reaction rate is observed at an electron energy of 24 eV. This may be due to the formation of atomic ions and nitrogen atoms in the primary process. The reaction-rate constant is proportional to the value of the nitrogen ionization function. The decisive role played by the ionization of nitrogen is also confirmed by experiments in which positive ions were removed from the reaction zone by a probe. Under these conditions the reaction rate decreases.

These results, and reaction kinetic data, suggest the following mechanism of oxide formation:

The main processes associated with the formation of chemically active particles are:

(1) $N_2 \xrightarrow{\sim} N_2^+ + e(N_2^{+*} + e, N_2^{++} + 2e)$.

(2) $N_2 \xrightarrow{\sim} N^+ + N + e(N^+ + N^* + e, N^{+*} + N^* + e)$.

(3) $N_2 \xrightarrow{\sim} N_2^* \rightarrow N^* + N(N^* + N^*)$.

(4) $N_2^+ + e \rightarrow N^* + N(N_2^+ + [e] \rightarrow N^* + N)$.

The most important reactions between active particles are:

(5) $N_2^+ + O_2 \rightarrow NO^+ + NO$.

(6) $N_2^{+*} + O_2 \rightarrow NO_2^+ + N$.

(7) $N_2^+ + O_2 \rightarrow N_2O^+ + O$.

(8) $N + O_2 \rightarrow NO + O$.

(9) $N + O_2 + M \rightarrow NO_2 + M$.

(10) $N_2 + O + M \rightarrow N_2O + M$.

Processes leading to the loss of active particles are:

(11) $N_2^+ + O_2^- \rightarrow \vec{N}_2 + \vec{O}_2$.

(12) $N_2^+ + O_2 \rightarrow N_2 + O_2^+$.

(13) $N_2^+ + NO \rightarrow N_2 + NO^+$.

(14) $N + N + M \rightarrow N_2 + M$.

(15) $N + NO_2 \rightarrow N_2 + O_2$.

(16) $N_2^+ + [e] \rightarrow \vec{N}_2$.

Our results show that for electron collisions (up to 100 eV) the probability of process (1) is about 10 times greater than that of process (2). The principal reactions between active particles are the processes (5), (6), (8), (9). The interaction and dissociation reactions of nitrogen oxides are not considered here. The reaction rate constant of equation (1) may be expressed thus:

$$K = \frac{K_0 \cdot J}{E_{kr}} \sqrt{\frac{K_1 RT}{\alpha MP}}\, e^{-\frac{7500}{RT}} \int_0^{E_{max}} F(E) q(E) dE \qquad (2)$$

where K_0 is the proportionality factor, J the radiation intensity, E_{kr} the ionization potential of nitrogen molecules, K_1 the effective constant for the production of chemically active particles, R the gas constant, T the temperature, α the ion recombination coefficient, M the molecular weight of hydrogen, P the pressure, $q(E)$ the ionization function of nitrogen, $F(E)$ the radiation energy distribution function, E_{max} the maximum energy of the ionizing particles.

Using equations (1) and (2), the relation between the oxidation process and the conditions and nature of the radiation can be analysed.

* Translated by L. C. RONSON from *Atomnaya Energiya* **3,** No. 10, 350 (1957).

Equation (2) was verified at the pressures 0·1 and 760 mm Hg, at electron energies of 20–400 eV and $2 \cdot 10^5$ eV, and at temperatures from 0 to 200°C. The reaction rate constant is independent of pressure if $\alpha \sim T/P$ (which applies at fairly low temperatures and pressures up to ~15 atm).

Table 1 lists some experimentally measured nitrogen dioxide yields for various radiation energies and other conditions. Data for electrical discharges are also given for comparison.

Table 1 shows that the greatest yields are obtained at fairly high temperatures and low pressures. This is connected with the competition between the elementary reactions which lead to the formation of nitrogen oxides, processes leading to the annihilation of active particles, and dissociation reactions of the oxides. The equilibrium NO_2 concentration for air irradiated with fast electrons (at 20–30°C) is 5·5–6 per cent. This concentration is considerably greater than the equilibrium concentration in a thermal reaction.

A change to the liquid phase and to low temperature does not appreciably affect the reaction yield.

When irradiating nitrogen dissolved in water, or nitrogen above water, the oxide yields per unit of absorbed energy are relatively small. Similar values were obtained by PROSKURNIN *et al.*[3] and HAISSINSKY *et al.*,[4] in oxidizing nitrogen with the radiolysis products of water in aqueous alkaline solutions.

It is clear from the table that a change from fast electrons to γ-rays in experiments at atmospheric pressure does not appreciably affect the reaction yields. Approximately similar yields have been obtained using a nuclear reactor.

WRIGHT *et al.*[5] irradiated air at atmospheric pressure above water and obtained a yield of approximately one fixed atom of nitrogen per 100 eV. PRIMAK and FUCHS[6] irradiated moist air at 1 atm and 40°C, and obtained a yield of 3 atoms per 100 eV. HARTECK and DONDES[7] obtained 2·5 NO_2 molecules per 100 eV at 140°C and 1 atm and 5 NO_2 molecules per 100 eV at 175°C and 25 atm. The reaction yield can obviously be increased by neutralization of the negative ions[8] or by sensitization of the nitrogen atom and ion forming processes. As yet there is no experimental evidence of yields greater than 6 NO_2 molecules per 100 eV. Such a yield corresponds to a consumption of 7000 kWh/ton of anhydrous nitric acid, about the same as in the ammonia process.

The radiation oxidation of nitrogen can only become economically important if use can be made of energy from nuclear fission, in a nuclear reactor. A complicating factor is that neutron capture by nitrogen, i.e. the reaction ${}_7N^{14} + n \rightarrow {}_6C^{14} + p$, has an adverse effect on the reactor operating conditions (the effective neutron capture cross-section of nitrogen is $\sigma_N \simeq 1{\cdot}5 \times 10^{-24}$ cm², that of oxygen $\sigma_0 \simeq 2{\cdot}8 \times 10^{-28}$ cm²). In principle nitrogen, which absorbs

TABLE 1

Radiation		Composition of mixture oxygen : nitrogen	Pressure (mm Hg)	Temperature (°C)	Reaction yield, NO_2 mole per 100 eV
Type of radiation	Energy (keV)				
γ-radiation	<1330	1 : 4	760	15–25	1·2
γ-radiation and fast electrons	200–1330	2 : 1*	760 liquid phase	15–25	0·1–0·3
Slow electrons	0·02–0·40	1 : 4	<0·1	~5	5 ÷ 6
Fast electrons	240	1 : 1	liquid phase	−183	1 ÷ 2
Fast electrons	200	1 : 1†	760	40–50	2
Fast electrons	200	1 : 4†	760	40–50	1·3
Fast electrons	200	0 : 1†	760	40–50	0·2
Fast electrons	200	1 : 4	760	15–25	1·5
Fast electrons	200	1 : 4	760	~200	3 ÷ 3·5
Silent discharge	<6	2 : 1	1	<50	2·5
High frequency discharge	<4	2 : 1	1	<100	4·0
High frequency discharge	<15	1 : 1	760	<200	1·7

* In saturated aqueous solution. † Above water.

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excess neutrons, can be used to control a nuclear reactor. This negative effect can be to some extent compensated by partly replacing the nitrogen by other neutron absorbers. The proton produced in the above nuclear reaction has an energy of ~600 keV. This can give about 10^4 ionizing events and, consequently, about 10^4 nitrogen dioxide molecules for each thermal neutron absorbed by the nitrogen.

Neutron capture can be reduced by increasing the proportion of oxygen in the gaseous mixture.

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A Simple Apparatus for the Production of Radiation-induced Mutations in Seed*

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Introduction

Plant breeders are essentially concerned with exploiting the variability which occurs in our cultivated varieties of crop plants or in their closely related varieties and species. They do this either by a process of selection from existing populations or by recombining and reshuffling characters by hybridization and selecting from the progeny. Among other things radiation provides an increased source of variability in plants exposed to it, and work on radiation induced mutation breeding has been going on in various institutes for several years. Promising varieties of cereals, peas, soyabean etc. with increased resistance to disease or higher yielding ability have been produced, of which some have already been released on the market.

The rate of occurrence of the so-called mutations can be increased from the spontaneous frequency of 1 in 10^5–10^7 to as high as 1 in 30. However, only one useful mutant may be produced for every 700–800 inferior ones. Hence a large number of plants must be handled in any program of mutation breeding.

Up to the present time, seeds have been the part of the plants to be most frequently treated. They are easy to handle, are not easily damaged and large numbers can be irradiated at once. The value of pollen irradiation or even whole plant irradiations is still in doubt.

There are many different types of ionizing radiation which can be used to induce mutations in plants viz. alpha-, beta-, gamma- and X-rays, neutrons and various charged particles. The difference in types of mutations obtained with the various radiations is remarkably small considering their totally different natures.

Practical considerations

The Department of Agriculture at the University of Pretoria has recently initiated a groundnut breeding program in which specifically immunity is being sought against the dreaded Rosette virus disease which is ravaging the groundnut crops in South Africa.

Suitable facilities exist in several overseas institutes for such irradiations. However, the cost of transporting such seed is considerable and there are serious difficulties connected with the import and export of agricultural products. Hence it was decided to execute these irradiations at the local National Physical Research Laboratory.

Quantities of seed of the order of 15 lb each, had to be irradiated to give a suitable number of individual seeds. The doses decided on by the geneticist ranged from 8000 to 21,000 rad. Only neutrons, gamma- and X-rays are sufficiently penetrating to make the uniform irradiations of this quantity of seed feasible. In South Africa the only apparatus which can possibly deliver a big enough neutron flux, is the C.S.I.R. cyclotron. However, considerable practical problems are presented in this case as regards dosimetry and uniform, reproducible

* Read before the Congress of the South African Genetic Society held in Pretoria from 22 to 24 July, 1958.

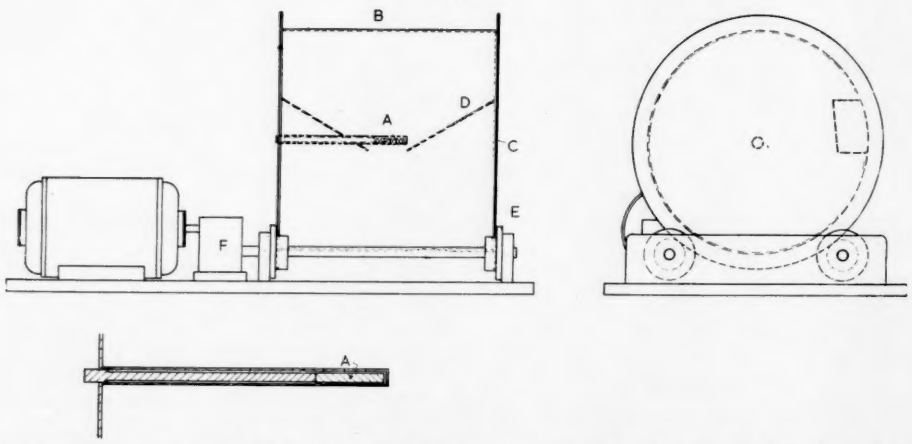

FIG. 1. Schematic diagram of the seed irradiation apparatus, showing the Co^{60} source *A*, the drum *B*, its lid *C*, the mixing fins *D*, the rotation wheels *E* and the driving mechanism *F*.

irradiations and it is also rather expensive to use for routine work. The use of X-rays was also decided against as the operation of conventional machines is too expensive and the dose distribution rather inhomogeneous due to the relatively soft radiation. Therefore, it was decided to attempt the use of a source of gamma radiation.

Development of apparatus

The radioisotope cobalt-60 emits penetrating gamma radiation and is, therefore, commonly used for such irradiations. The usual arrangements employ either a big source at a distance from the sample to be irradiated, or a number of smaller sources surrounding the sample. Both of these methods give a quite uniform dose distribution but require activities of the order of 100 c.

The most active source available was only of about 1 c strength (as used in industrial radiography). This activity is, of course, completely inadequate to deliver the required dose (over 20,000 rad) to the large volume (about 7 l.) of seed in one of the conventional ways within a reasonable time. However, if we remember that 1 c Co^{60} gives 1·3 rad/hr at 1 m, i.e. 130 rad/hr at 10 cm and 13,000 rad/hr at 1 cm, it is clear that such doses can be delivered if the source is surrounded by the seed. Uniformity of irradiation of the individual seeds may then be ensured by continuous rotation of the seed container.

A simple apparatus was, therefore, designed and built, consisting of a drum of about 25 cm diameter and 25 cm length with a re-entrant tube in the centre, into which the Co^{60} source could be placed (Figs. 1 and 2). After the correct quantity of seed had been placed in the drum (which is only about 90 per cent filled to ensure good circulation) the source is placed in the centre by means of remote handling tongs, where it is kept in position by a suitable pin. The radiation hazards attached to this procedure are small. The whole drum is then rotated in a simple way at about 10 rev/min.

Dosimetry

On account of the rather uncertain and complicated calculations involved, the dose delivered was determined experimentally in two separate ways i.e. with the Fricke dosemeter[1] and film from the Film Badge Service.

The Fricke dosemeter consists of a solution containing ferrous sulphate, and the oxidation of ferrous to ferric by the radiation is then an absolute measure of the dose received. The ferric concentration was determined in a conventional spectrophotometer at a wavelength of 305 μ and a *G*-value, for the radiation oxidation process, of 15·5 assumed. The inside of the drum was coated with a suitable plastic to prevent any interaction of the drum material with the dosemeter solution. As the bulk density of the seed was close to one (1·05), the drum was then filled with the Fricke solution and after sufficient exposure a sample of the stirred solution gave the average dose received.

In the second method, small sample holders, similar in size and material to the seeds were made up so that small pieces of a standard film could be placed in them. These were mixed with the seed during irradiation but using a smaller source, and the blackening of the film then served as measure of the dose. Also, the individual variations gave an indication of the degree of uniformity with which the individual seeds were irradiated.

Good agreement was obtained with both methods

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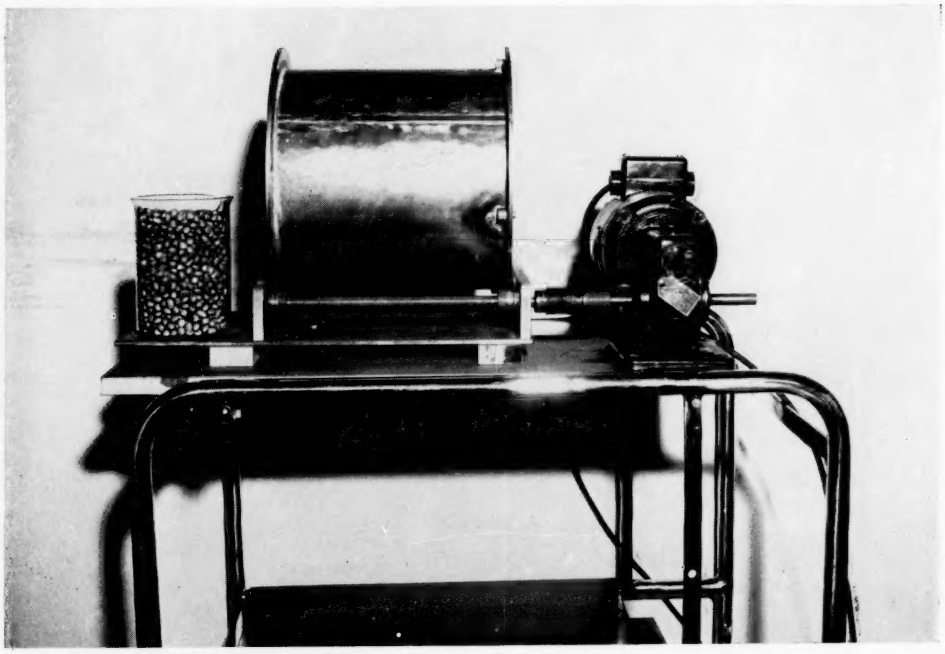

FIG. 2. Photograph of open seed container showing mixing fins and re-entrant tube containing source.

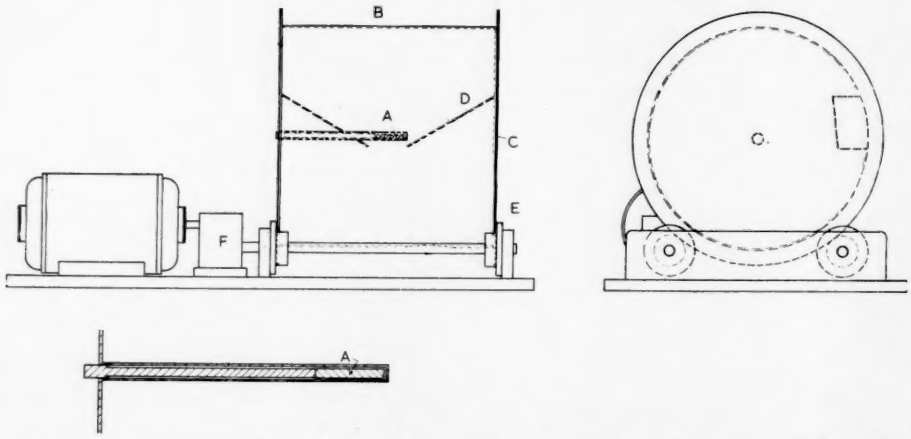

FIG. 1. Schematic diagram of the seed irradiation apparatus, showing the Co^{60} source *A*, the drum *B*, its lid *C*, the mixing fins *D*, the rotation wheels *E* and the driving mechanism *F*.

irradiations and it is also rather expensive to use for routine work. The use of X-rays was also decided against as the operation of conventional machines is too expensive and the dose distribution rather inhomogeneous due to the relatively soft radiation. Therefore, it was decided to attempt the use of a source of gamma radiation.

Development of apparatus

The radioisotope cobalt-60 emits penetrating gamma radiation and is, therefore, commonly used for such irradiations. The usual arrangements employ either a big source at a distance from the sample to be irradiated, or a number of smaller sources surrounding the sample. Both of these methods give a quite uniform dose distribution but require activities of the order of 100 c.

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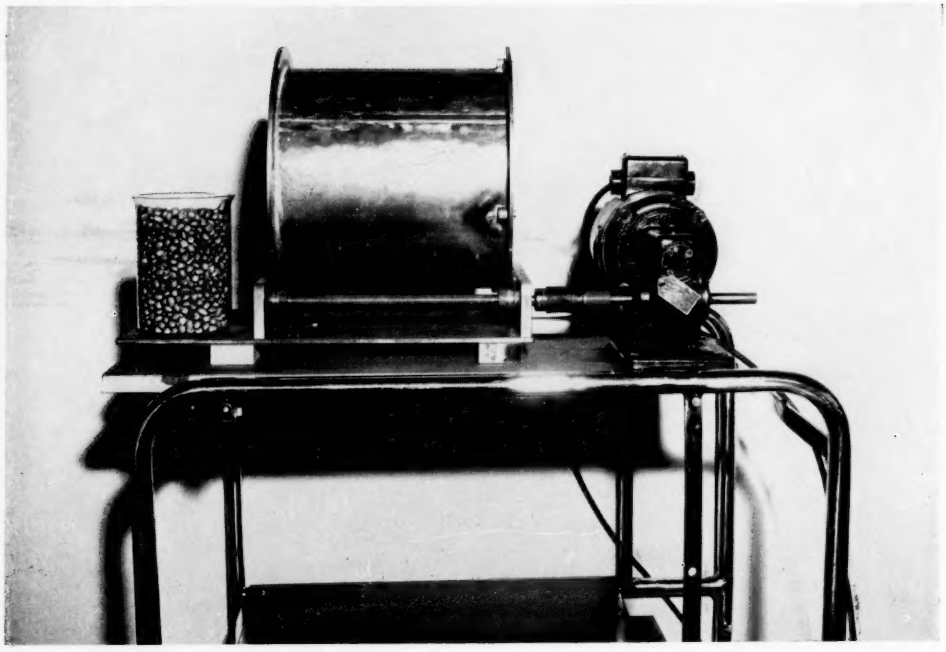

FIG. 2. Photograph of open seed container showing mixing fins and re-entrant tube containing source.

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for the delivered dose rate and it was also found that the standard deviation of individual doses was within the experimental error.

Conclusions

This method of irradiation is very convenient, simple and dependable for the delivery of doses up to 25,000 rad to large volumes of seed up to 20 lb in weight using only 1 c of Co^{60}. In our set-up we obtained a dose rate of 110 rad/hr with a 700 mc Co^{60} source, and it was, therefore, possible to give the maximum dose required (21,000 rad) in about one week. (Such low dose rates may, however, give quite different radiation effects to high dose rates c.f. especially on dry seed, CURTIS *et al.*[2].) When other volumes have to be irradiated other sizes of drums will be required. Although the health hazards involved are rather small when done by a qualified person, it is doubtful whether stronger sources can be used in this way.

Five batches of groundnut seed have been given doses varying from 8000 to 21,000 rad in this way and then planted out. The somatic radiation effects appeared as expected and we are now looking forward to the results of the subsequent breeding program.

Acknowledgement—This paper is published with the permission of the South African Council for Scientific and Industrial Research.

J. K. BASSON*

National Physical Research Laboratory
Council for Scientific and Industrial Research
Pretoria, Union of South Africa

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2. CURTIS H. J., DELIHAS N., CALDECOTT R. S. and KONZAK C. F., *Radiation Research* **86,** 526 (1958).

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A Method for Increasing the Contrast and Definition of Scintigrams*

(*Received* 15 *August* 1958)

AFTER reviewing a number of scintigrams obtained with the thyroid scintiscanner developed by CASSEN *et al.*,[1] a modification of the equipment was designed in order to improve the contrast and definition of thyroid scintigrams. The printer of our scanning apparatus was made to respond to the counting rate detected by the tube in a non-linear fashion. At low counting levels corresponding to background the printer was made to operate not at all. In areas corresponding to active thyroid tissue the printer completely blackened the paper. In an area of an inactive nodule within the thyroid gland, the printing rate was slowed sufficiently to clearly delineate and label the nodule as non-active.

The modification (Fig. 1) in our equipment was carried out as follows: A neon tube oscillator circuit was coupled to a vacuum tube amplifier and made to cause a relay to follow the neon tube. The scintillation counter tube was fed into a ratemeter.† The output of the ratemeter was used to close a relay via a transistor amplifier circuit. When this relay closed, the printer was activated at the same rate as the flashing neon tube, which was fast enough to blacken the paper. A sensitivity control was provided which allowed the response to be adjusted according to the level of radioactivity in the patient. The circuit described is similar in principle to the background cutoff scheme mentioned below but differs from it in that no scaler was used, the neon oscillator circuit taking its place.

A number of other similar projects have been undertaken. CURTIS in 1952 suggested a method for speeding up and improving the contrast of thyroid scintigrams.[2] This amounted to a background cutoff circuit that would render the printer inoperative as long as the counting rate was under a certain preset critical level. Later a "contrast amplifier" was experimentally tested by the Reed-Curtis Company. This device either adds or subtracts counts at the wish of the operator. Thus, it is possible to "subtract background," and to print only pertinent information. More recently MCINTYRE[3] has published results using a background cutoff type circuit in conjunction with scintigrams of the liver.

Photographic methods of scanning are also available. Due to the characteristics of film and the incandescent light used to expose the film, a blackening is possible that is non-linear, and the contrast of the resulting scintigram is much greater than that of conventional scintigrams. However, the method requires cumbersome photographic procedures and expensive equipment.

The circuit as described above was used with a number of patients who were also scanned in the conventional manner. The results are compared in Figs. 2 and 3.

* From the Department of Radiology, School of Medicine, University of California at Los Angeles.

† Radiation Sentinel Ratemeter manufactured by the Nuclear Instrument and Chemical Company.

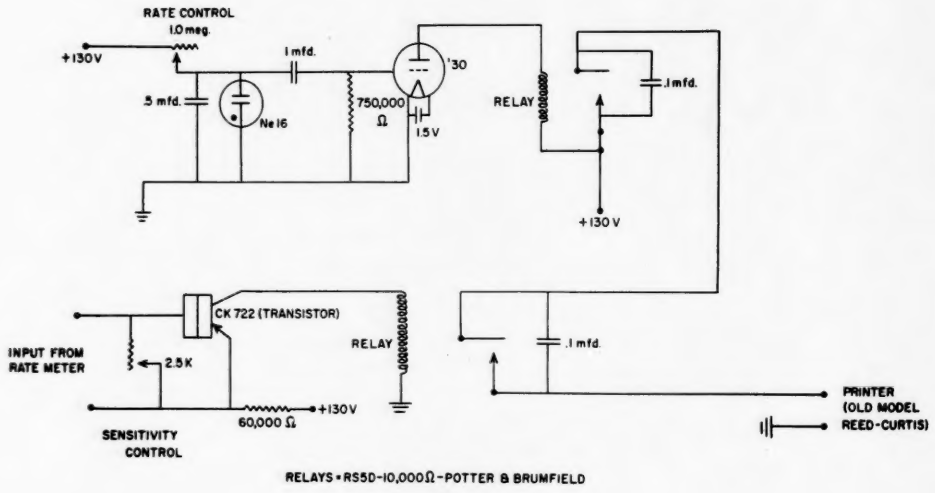

FIG. 1. Circuit diagram

Discussion

After preliminary trials with the neon oscillator circuit, the following observations were made of the response of the printing circuit to the counting rate. Due to the random nature of the counts, values near the threshold level as set by the sensitivity control occasionally activated the printing circuit. The nearer to the threshold level, the more frequently this occurred. This results in a gradient in shades between black and white. The response to a very slight increase in radioactivity resulted in a very great increase in darkness. The response is apparently non-linear and yields far greater contrast than conventional equipment.

Summary

A simple, inexpensive neon tube oscillator circuit is presented which will increase the contrast and present more strikingly the information gained from scanning the thyroid gland. The use of a scalar is eliminated. Examples are shown.

Acknowledgement—Appreciation is expressed to Dr. L. W. BENNETT and his staff for encouragement and help.

05701249, 14 Field Hospital
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1. CASSEN B., CURTIS L., REED C. and LIBBY R. L., *Nucleonics* **9,** No. 2, 46 (1951).
2. CURTIS L., *Note on a method for the speeding up and improving the contrast of thyroid scintigrams.* Atomic Energy Project, University of California, Los Angeles. Paper No. 196 (1952).
3. FREIDELL H. I., MACINTYRE W. J. and REJALI A. M., *Amer. J. Roentgenol.* **77** No 3, 455 (1957).

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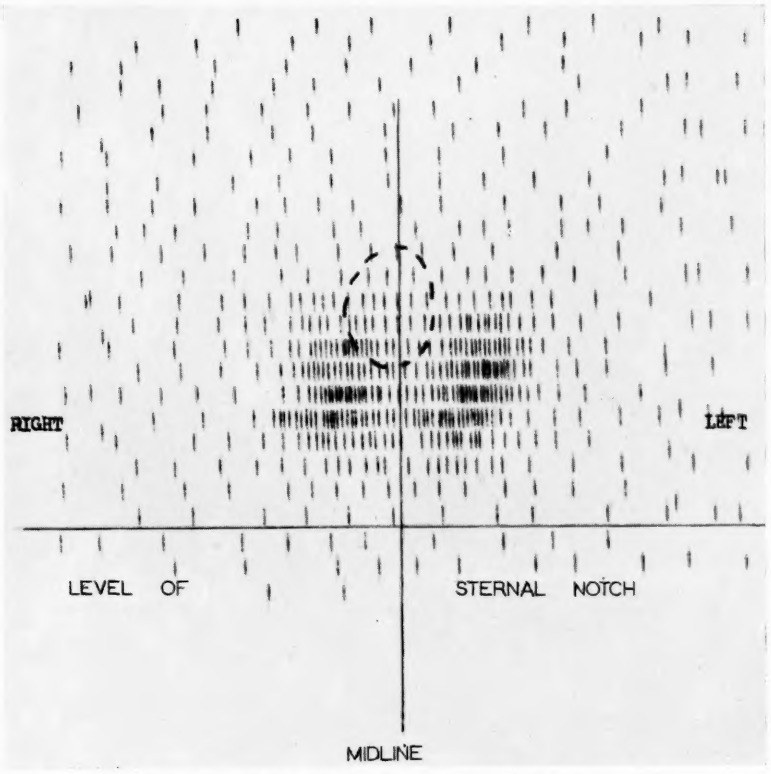

FIG. 2a. Scan of thyroid gland containing an inactive nodule using conventional methods and equipment (nodule circled).

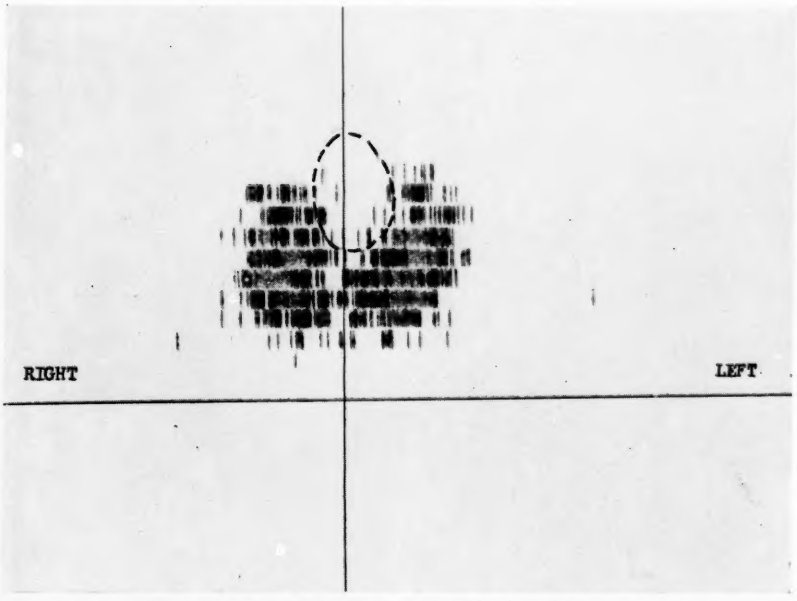

FIG. 2b. Same as Fig. 2a using modification of apparatus described in text.

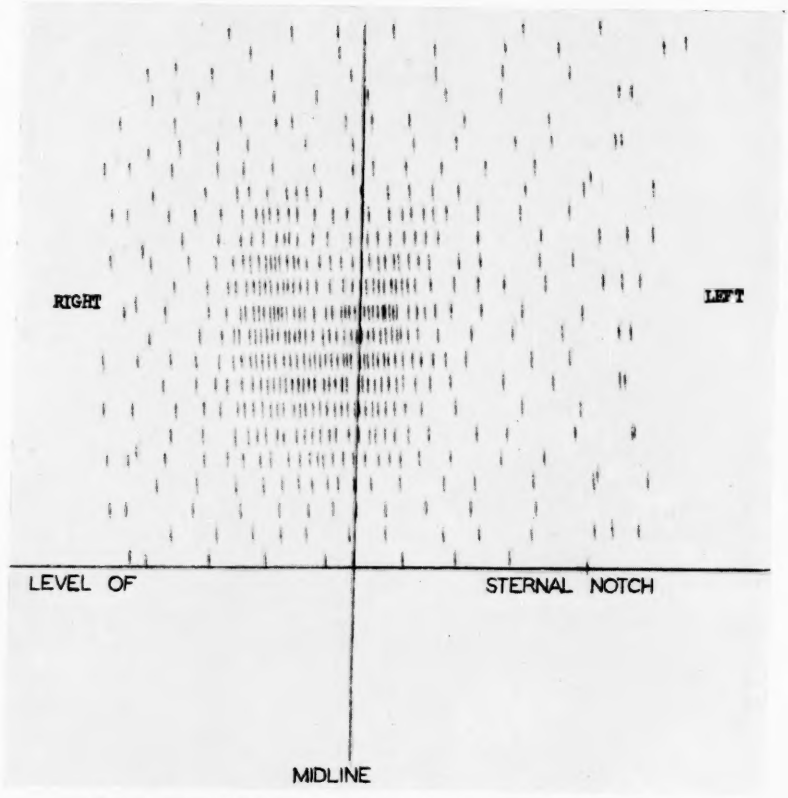

FIG. 3a. Scan of enlarged thyroid gland using conventional methods.

FIG. 3b. Same as Fig. 3a using modification of apparatus described in text.

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international news

A E C OFFICE OF ISOTOPES DEVELOPMENT

The Atomic Energy Commission has recently established an Office of Isotopes Development. The new Office develops over-all policy and procedures and administers programs for encouraging the growth and development of radioisotope and radiation uses in industry. It also administers the AEC radioisotope production, marketing and sales program. The Isotope Development Program of the Office encompasses the following activities:

1. *Isotope Applications Development*

Encourages industry to develop new and exploit known uses of radioisotopes and nuclear radiation and nuclear radiation and supports research and development in industrial applications.

2. *Industrial Process Radiation*

Encourages and supports accelerated research and development of economic application of high-intensity radiation to industrial processes.

3. *Industrial Isotope Technology Training*

Increases availability to industrial personnel of training and education necessary for practical and safe applications of radioisotopes and radiation in industry.

4. *Industrial Isotope Production*

Assures availability of required quantities of radioisotopes at economic prices for large-scale industrial use, and encourages their production by private enterprise.

The Office of Isotopes Development advises private groups on opportunities open to them in radioisotope applications and assists industry in obtaining information, materials and services needed in the development of their isotope programs. It also arranges for orientation seminars and special meetings concerning radioisotope applications. It has neither regulatory nor inspection functions. These are assigned to the AEC Division of Licensing and Regulation.

The Office is located in Commission headquarters, Germantown, Maryland. Correspondence should be addressed to:

Dr. Paul C. Aebersold, Director
Office of Isotopes Development
U.S. Atomic Energy Commission
Washington 25, D.C.

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book reviews

Nuclear Masses and Their Determination. Edited by PROF. H. HINTENBERGER. Pergamon Press, London, New York, 1957. 267 pp. 84s.

THE book is the report of the second conference on the precise determination of atomic masses held in honour of Professor JOSEF MATTAUCH at Mainz in July 1956. Each paper presented is reproduced together with some of the ensuing discussion.

The book is divided into eight sections. Great advances in atomic mass determination have been made since the first conference in Washington in 1951 and many of the inconsistencies of a given method have been reduced or removed. A detailed review of this progress up to 1956 and an introduction to the papers is given by K. T. BAINBRIDGE in Section I.

Section II is concerned with systematics and consists of papers by A. H. WAPSTRA, U. CAPPELLER and K. WAY. The latest data on binding energies are graphically represented and the regularities examined in the light of the shell model. The new data are seen to improve the earlier curves and are remarkably self consistent. The papers in Section III deal exclusively with recent mass spectroscopic results. A. O. NIER *et al.* describe recent work in the University of Minnesota using the doublet method with their new double focusing spectrometer. New values are presented for the secondary mass standards H^1; D^2; C^{12} and S^{32}. Other masses are determined in the range $1 \leqslant A \leqslant 70$ and these are compared with nuclear reaction determined values. NIER discards certain Q values which are not self consistent and succeeds in somewhat improving the agreement between nuclear reaction values and the mass spectrometer values. Similar results in the region xenon to europium, obtained in the University of Minnesota, are presented by W. H. JOHNSON and A. O. NIER. The Canadian measurements at McMaster in the region iron–nickel–zinc are given by H. E. DUCKWORTH *et al.*, who have also investigated the pressure dependence of doublet spacings in their spectrometer. Finally the recent results of L. G. SMITH using his new mass synchrometer are listed.

The derivation of nuclear masses from nuclear reactions is to be found in Section IV. The principles of the most common methods for measuring reaction energies, and their limitations are described by W. W. BUECHNER. Atomic masses in the region sulphur to titanium, determined from Q value measurements of many authors, are calculated by P. M. ENDT, starting from the mass spectrometer measurement of S^{32} by K. S. QUISENBERRY *et al.* His results are compared with the well known list due to WAPSTRA. Recent nuclear reaction Q value measurements in the important region around S^{32} are presented by D. M. VAN PATTER *et al.* Disintegration energies, measured by β-and γ-ray spectrometry, are described by A. C. G. MITCHELL who outlines the techniques involved and shows how it is possible to obtain a cross check on the validity of decay schemes when two different radioactive parents produce the same daughter nucleus. Certain mass differences obtained for neighbouring isobars are listed.

In Section V the results obtained by these two principal approaches are critically compared. Professor MATTAUCH deals with the light nuclei (H^1 to S^{32}). He has examined 196 nuclear reaction data and performed a least squares analysis on 70 atomic masses derived from the various Q values. He shows his adjusted masses and errors plotted alongside WAPSTRA's figures (which in the main are in agreement) and the recent masses of NIER *et al.* and L. G. SMITH. The mass spectroscopic figures continue to lie outside the errors of the adjusted Q masses. By further examination of the reaction cycles, MATTAUCH selects seven reactions as being suspect; alteration of the Q values of these reactions on the basis of mass spectroscopic data and re-evaluation of the least squares masses leads to much closer agreement with the mass spectrometer figures as a whole. D. M. VAN PATTER approaches the problem from the aspect of reaction data. Whilst agreeing that some Q values may need review he shows that a systematic error in the mass spectrometer measurements could be cumulative when arriving at the mass of S^{32} (the most important isotope at present where there is a discrepancy between the methods).

The newest technique for measuring mass differences from microwave spectra is described in Section VI by S. GESCHWIND. He describes the correlation between isotope shift in rotational frequency and the mass change. The errors in the method are fully discussed and a list of mass ratios is presented.

Section VII is devoted to the description of several of the newer instruments in use or under construction.

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These include the spectrometer at Minnesota; a stigmatic focusing spectrograph in Munich; and the large double focusing mass spectrograph at Osaka. In addition spectrographs under construction at Harvard University and McMaster University are described. Two other interesting spectrometers are also discussed; a magnetic and an electrostatic time of flight instrument. Both machines have novel features. (A plate belonging to the magnetic instrument seems to have found its way to face page 250). SMITH's synchrometer was not described in his absence.

The final section (VIII) contains remarks on the adjustment of double focusing spectrographs and on the precision of spectral line position measurements. There is also a discussion on secondary mass standards for the range $A > 30$. H. E. DUCKWORTH examines the desirable features of such secondary standards and suggests some atoms as being suitable.

Marked discrepancies still occur between masses calculated from data obtained by different methods. This book does much to explain and correlate these discrepancies and to show methods by which they may be reduced. The critical evaluation and comparison of the two main experimental approaches in Section V is especially valuable in pointing the way to further research. A very large number of references are given throughout the volume which helps to fill in the gaps which are inevitable in Conference Proceedings. The book unfortunately has no index.

R. A. ALLEN

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BOOKS RECEIVED

RICHARD G. FOWLER and DONALD I. MEYER. *Physics for Engineers and Scientists*. 546 pp. (Allyn and Bacon Inc. 1958) $8.00.

A. LACASSAGNE and G. GRICOUROFF. *Action of Radiation on Tissues* (translated by CLARENCE C. LUSHBAUGH and GRETCHEN R. RIESE). (Grune and Stratton Inc. 1958) $6.25.

forthcoming papers

H. J. M. Bowen: The determination of gallium and molybdenum in biological material by activation analysis.

Milton G. Crane, John E. Holloway, James McEachen, Charles Sears and Ronald Selvester: Localization of intracardiac shunts using instantaneous injection of RISA with two-site sampling.

E. H. Graul and H. Hundeshagen: Investigations of radio-yttrium (Y^{90}) metabolism. Studies of organ-distribution with special regard to the radio-autographic method of demonstration and to paper electrophoresis under various experimental conditions.

A. A. Zhoukhovitsky: Use of radioactive isotopes in investigations of the diffusion and thermodynamic characteristics of solid solutions.

Knut Ljunggren, Lars-G. Erwall, Jan Rennerfelt and Torbjörn Westermark: Tracing of water flow by means of radioactive isotopes and scintillation counters.

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Erratum

Int. J. Appl. Rad. Isotopes **4,** 30 (1958)

An Examination of Lubrication with Soap, using Radioactive Sodium Stearate

G. W. Rowe (joint author with J. Golden and P. R. Lancaster) is wrongly given as G. R. Rowe.

Publisher's Notice to Subscribers and Contributors

Due to unexpected production difficulties which occurred in the summer of last year, various issues of the *Journal of Applied Radiation and Isotopes* suffered delay in publication. These difficulties have now been surmounted and the *Journal* is now appearing regularly.

Papers accepted for publication by the Editors are now published within four months of acceptance. Technical Notes are given priority and are published within 30 to 60 days.

Volume 6 of the *Journal*—to be published in May 1959—will consist of a summary report and proceedings of the FAO European Meeting on the use of ionizing radiations for food preservation held at Harwell, England, in November 1958. The table of contents of this volume will be published in Volume 5, Number 2.

International Journal of Applied Radiation and Isotopes, 1959, Vol. 5, pp. 77–88. Pergamon Press Ltd. Printed in Northern Ireland

The Use of a Test-therapy Dose of Radio-iodine for Thyrotoxicosis*

T. H. ODDIE,† F. F. RUNDLE‡ and I. MESCHAN§

(*Received* 15 *October* 1958)

A new approach is made to the I^{131} therapy of thyrotoxicosis. In 125 patients the response to therapy has been followed quantitatively with serial I^{131} uptake tests.

To avoid post-therapy myxoedema, a safe upper limit has been found for a first "test-therapy" dose, based on the initial level of thyroidal activity and on the approximate gland size.

Depending on individual sensitivity, a patient may be brought down either to a euthyroid state, or to a lower hyperthyroid level by this "test-therapy" dose. The response to a later dose is then predictable to a useful extent from the results of the first dose, so that a second dose, if necessary, will prove definitive in most cases.

A suggested dosage schedule is given.

L'EMPLOI D'UNE DOSE ÉPREUVE-THÉRAPEUTIQUE DE RADIO-IODE POUR LA THYROTOXICOSIE

Une nouvelle approche se fait à la thérapie employant I^{535} pour la thyrotoxicosie. Chez 125 patients la réponse à la thérapie a été suive quantitativement avec des essais en série de l'absorption d'iode 131.

Afin d'éviter la myxoedéma suivant la thérapie, on a trouvé une limite supérieure sûre pour une première dose "épreuve-thérapeutique," fondée sur le niveau préalable d'activité thyroide et sur la grandeur approximative de la glande.

Selon la sensibilité individuelle, on peut réduire un malade soit à une condition euthyroide soit à un niveau hyperthyroide inférieur par cette dose "épreuve-thérapeutique". Une prédiction utile de la réponse à une dose suivante peut être faite des résultats de la première dose, de sorte qu'une seconde dose, si telle est nécessaire, sera rendue définitive en la plupart des cas.

On rend un schéma de dosage proposé.

ПРИМЕНЕНИЕ ПРОБНОЙ ТЕРАПЕВТИЧЕСКОЙ ДОЗЫ РАДИОАКТИВНОГО ИОДА ПРИ БОЛЕЗНИ ЩИТОВИДНОЙ ЖЕЛЕЗЫ

Разработан новый метод лечения болезни щитовидной железы с помощью I^{131}. Количественная проверка такого лечения у 125 пациентов производилась путем последовательного определения поглощения I^{131}.

Во избежание пост-терапевтической миксодемы, на основе исходного уровня активности щитовидной железы и ее приблизительных размеров, был установлен безопасный верхний предел пробной терапевтической дозы.

Такая пробная терапевтическая доза доводит пациента либо до нормального состояния щитовидной железы, либо до низшего гипертироидного уровня, в зависимости от чувствительности данного индивидуума.

Таким образом по действию первой дозы можно предсказать в утилитарно-оправданных пределах действие второй дозы, так что последняя, если она вообще необходима, будет в большинстве случаев эффективна.

Приводится предагаемая длозировочная таблица.

* Work partly done in the Joan Bonamy Research Laboratory and supported by a generous grant from an anonymous donor.

† Formerly Associate Professor of Physics, Department of Radiology, Bowman Gray School of Medicine, Winston-Salem, North Carolina. Now Research Physicist, Unit of Clinical Investigation, Royal North Shore Hospital, Sydney, Australia.

‡ Head of Unit of Clinical Investigation and Surgeon, Royal North Shore Hospital, Sydney, Australia.

§ Professor and Head, Department of Radiology, Bowman Gray School of Medicine, Winston-Salem, North Carolina.

DIE VERWENDUNG EINER TEST-THERAPIE-DOSIS VON RADIOJOD BEI THYROTOXICOSE

Ein neuer Weg der J-131-Therapie bei Thyrotoxicose wurde versucht. Bei 125 Patienten wurde das Ansprechen auf die Therapie durch J-131-Aufnahmetests quantitativ verfolgt.

Um post-therapeutische Myxödeme zu vermeiden, wurde zunächst die unschädliche obere Grenze für die erste "Test-Therapie"-Dosis ermittelt, wobei die Ausgangs-Schilddrüsen-Aktivität und die Grösse der Drüse als Mass verwendet wurden.

In Abhängigkeit von der individuellen Empfindlichkeit kann der Patient durch diese "Test-Therapie"-Dosis entweder zur normalen Schilddrüsentätigkeit oder auf einen Zustand niedrigerer Überfunktion gebracht werden.

Das Ansprechen auf eine spätere Dosis lässt sich aus den Ergebnissen der ersten Dosis in verwendbarem Ausmass voraussagen, so dass, falls eine 2. Dosis sich als nötig erweist, diese in den meisten Fällen endgültig genügt. Eine Tabelle für die vorgeschlagenen Dosisgrössen wurde angegeben.

INTRODUCTION

THE problem of prescribing the appropriate dose of radio-iodine for the treatment of thyrotoxicosis is usually well appreciated by those interested in this disease. Too small a dose delays effective treatment; too large a dose results in myxoedema.

It has often been assumed that the I^{131} retained is distributed homogeneously throughout the thyroid gland, so that the radiation dose in roentgens[1] is calculable from physical principles using a reliable estimate of the size[2,3] of the gland. Unfortunately the I^{131} distribution is not homogeneous[4] so that the dosage distribution also will be very irregular.[5] Moreover, size estimates may be inaccurate,[6] although better results may become obtainable if scintillation scanning[7,8] devices are further improved.

Because of these difficulties, several workers[9,10] have reverted to an empirical dosage schedule, using a fixed amount of I^{131}, modified sometimes by a millicurie or two in individual cases.

Published results show a disappointingly high incidence of myxoedema, as high as 12 per cent or more[8,10,18,19] amongst patients treated on either of the above plans. In contrast, a lower incidence of myxoedema, with, however, a protracted treatment time, is obtained by a multiple, small dose technique such as that described by GORDON and ALBRIGHT.[11]

This paper describes the results of treating 125 patients with I^{131} in the period 1955 to June 1958. During this period, the plan of treatment was modified. To begin with, a system of multiple, small, approximately equal doses was used. Experience with this led to the adoption of a new method, as follows:

(1) The patient is given an initial "test-therapy" dose related to the thyroidal uptake rate and to the approximate gland size. Based on experience, this dose is cautious, and is quite unlikely to cause myxoedema; at the same time it will produce significant improvement in most cases.

(2) The response to the first dose is measured by further I^{131} tracer measurements and enables radio-resistant glands to be distinguished and controlled without delay by a second dose, related quantitatively to their radio-resistance.

METHODS

Serial tracer observations were made, by methods described elsewhere[12,13] on all patients included in this report, to follow their thyroidal status as treatment progressed. These tests gave values of k_1 and k_2, the fractions of iodide circulating in the

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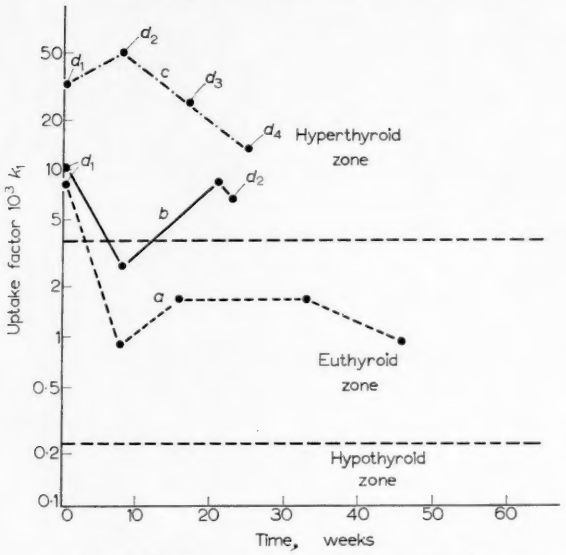

FIG. 1. Different types of response to I^{131} therapy.
Curve *a* Fall to approximately constant level with single dose d_1.
Curve *b* Rebound type of response to dose d_1.
Curve *c* Failure to respond to small first dose d_1, with positive response to larger following doses.

plasma iodide pool, that are cleared each minute by the thyroid gland and the kidneys respectively.

The value of k_1 provided a numerical measure of thyroidal status before treatment, and at follow-up times scheduled for 8, 21, 34 and 52 or more weeks after the last therapy dose of I^{131}.

Fig. 1 illustrates the several types of response found in different patients. Curve *a* is the ideal response in which the uptake rate k_1 falls to a euthyroid level and stays approximately constant after therapy; curve *b* shows the rebound type of response found[16,17] in about 40 per cent of all patients; and curve *c* shows the failure to respond to the first dose of I^{131} in a patient relatively insensitive to this form of treatment.

Assuming[14] that the fraction of I^{131} retained from a therapeutic dose of D mc is the same as for the preliminary tracer dose, the dose retained d mc, is given by

$$d = \frac{k_1 D}{k_1 + k_2} \qquad (1)$$

If the first and successive therapy doses retained are d_1, d_2 and so on, it is obvious that d_1 should be as large as possible without causing avoidable hypothyroidism in a significant number of the patients. However, there was no clear basis available for the selection of the best d_1 for many of the patients, particularly the earlier ones; for these d_1 was arbitrarily chosen as a cautious, low value.

If clinical assessment and a tracer I^{131} test 8 weeks after therapy showed that insufficient response had been obtained, or if k_1 relapsed to a hyperthyroid level at a later follow-up time, an additional therapy dose was given. In the earlier cases this dose, d_2, was about the same size as d_1 but as it became apparent that the response to repeated doses is approximately predictable from the effect on k_1 of the first "test-therapy" dose, the size of d_2 and any subsequent doses were modified accordingly.

For the numerical comparison of the response to therapy of different patients, or to different doses in the same patient, a sensitivity factor K has been used.

This is defined by the equation

$$Kd = \frac{k_a - k_b}{k_b} \qquad (2)$$

where k_a is the initial value of the thyroidal uptake rate factor k_1 before the therapy dose d, and k_b is the corresponding value after therapy. This equation is quite empirical, but it does give the correct answers for $d = 0$, and for $d = \infty$.

If duplicate determinations of k_1 were available the mean values were used for k_a or k_b, except in patients showing a definitely greater k_1 at 21 weeks after therapy than at 8 weeks; in these cases the 8-week observation was neglected. In collecting these data, care was taken to exclude any patients whose thyroidal status could have been confused by the recent ingestion of anti-thyroid drugs, thyroid extract, or other thyroid-affecting materials.

RESULTS

Tables 1 and 2 show the numerical results obtained in a series of 125 patients; those numbered A1 through A34 were treated in Winston-Salem with I^{131} from the Atomic Energy Commission at Oak Ridge, and those numbered 1 through 91 were treated in Sydney with I^{131} from the Atomic Energy Research Establishment at Harwell, procured through the Commonwealth X-ray and Radium Laboratory, Melbourne.

Regular comparisons have been made of the actual millicuries obtained from the above two suppliers using a mock-I^{131} reference source[15] calibrated by the National Bureau of Standards. All of the doses tabulated have been corrected to the United States millicurie; this required the multiplication of the nominal Sydney doses by a factor of 0·79.

All patients are listed in Table 1, with details of their thyroid disease and the type and approximate size of goitre, which was classed in five broad categories—0 nil, 1 small, 2 medium, 3 large, 4 very large. Also given are the dose in millicuries of I^{131}, the k_1 values observed, the sensitivity factor K calculated from equation (2), and the duration of follow-up. For multiple-dose patients this is the follow-up after the last therapy dose, and the K is a mean value.

Table 2 gives further data on the effects observed with repeated doses. In the sixth column the values of K are the mean ones used, as described below, for predicting the response to the next therapy dose; the remaining columns compare, as a ratio, the predicted value of k_1 with the actual value obtained after therapy.

After each individual dose, K was calculated from equation (2); when two doses were given the mean sensitivity K_m was found by the formula

$$K_m(d_1 + d_2) = \frac{k_a - k_b}{k_b} + \frac{k_b - k_c}{k_c} \qquad (3)$$

where k_c is the observed mean uptake rate k_1 after the second therapy dose d_2.

Equation (3) was extended in a similar way if more than two doses were given.

Finally, a comparison of the K observed for each repeated dose against the mean K_m found for earlier doses in the same patient showed, on the average, a significant increase in K with successive doses.

If f is the ratio of the observed K to the previous mean K_m, $\log_{10} f$ has a mean value of 0·281 for the 47 observations in Table 2. The standard deviation of this mean is $\pm 0{\cdot}078$ so that $\log_{10} f$ differs significantly from zero. The corresponding mean f is 1·91, which has been rounded off to $f = 2$. It follows then that the response to a second dose is to be predicted by modifying equation (2) to give

$$\frac{k_b - k_c'}{k_c'} = fK_1d_2 = 2K_1d_2 \qquad (4)$$

where K_1 is derived from the response to the first dose, and k_c' is the predicted value of k_c.

The predicted values of k_1 in the seventh column of Table 2 were derived in the above way. In those cases of totally inadequate dosage, where either equation (2) or equation (3) gave a negative value of K or K_m, no prediction was made for the result of the next dose.

TABLE 1. Sensitivity of response to therapy in different patients

Case No.	Goiter		Dose retained (mc)	Uptake rate factor $10^3 k_1$		Sensitivity K	Follow-up time in weeks
	Type†	Size		Initial	Final		
A1	H	0	2·07	3·77	0·96	1·4	33
A2	N	2	*	3·75	*	0·13	53
A3	D	1	*	4·09	*	2·6	22
A4	H	0	1·84	4·14	2·32	0·43	32
A5	N	2	2·62	4·19	2·76	0·20	34
A6	H	0	1·68	4·21	1·03	1·8	47
A7	N	3	3·05	4·3	2·42	0·26	34
A8	D	2	*	4·36	*	0·51	9
A9	D	1	2·97	6·4	5·36	0·06	22
A10	N	2	2·98	6·54	1·87	0·84	52
A11		2	*	6·72	*	0·05	24
A12	H	0	3·65	6·8	2·04	0·56	58
A13			4·16	6·88	0·22	7·3	34
A14	R	1	2·9	6·9	1·40	1·4	74
A15	R	2	1·91	7·2	3·80	0·47	12
A16	N	2	3·07	7·8	1·68	1·2	72
A17	D	2	2·70	8·2	1·29	2·0	46
A18	H	0	*	10·3	*	0·61	13
A19	D	3	*	10·6	*	0·43	34
A20	H	0	2·69	11·7	2·79	1·2	49
A21	H	0	3·41	11·8	1·06	3·0	52
A22	N	2	*	12·0	*	0·55	22
A23	H	0	3·30	12·2	1·28	2·6	47
A24	D	1	*	14·0	*	0·32	24
A25	D	1	2·25	17·2	2·38	2·77	115
A26	D	1	2·70	18·2	0	High	39
A27	D	1	*	22·0	*	0·50	48
A28	N	3	*	26·5	*	0·09	12
A29	D	3	*	27	*	0·00	10
A30	R	0	*	33·9	*	0·18	19
A31	R		4·0	35	1·48	5·7	43
A32	N	1	2·65	3·92	1·00	1·1	62
A33	D	3	3·58	34·0	3·7	2·3	34
A34	N	1	2·76	35·0	13·2	0·60	26
1	N	3	1·80	1·89	2·21	−0·08	45
2	N	3	*	3·02	*	−0·03	21
3	D	2	1·73	4·00	3·08	0·17	56
4	N	2	6·32	4·26	2·91	0·07	50
5	R	0	1·38	4·45	1·56	1·34	24
6	D	1	2·23	4·60	2·73	0·31	52
7	H	0	2·28	4·67	3·67	0·12	35
8	D	1	1·95	4·77	3·38	0·21	52
9	H	0	2·04	5·04	1·90	0·81	23
10	D	1	2·12	5·33	5·07	0·02	52
11	H	0	*	5·69	*	0·04	20
12	N	2	2·83	5·99	2·34	0·55	52
13	R	1	*	6·02	*	0·73	9
14	D	1	2·25	6·07	2·70	0·55	29
15	D	2	1·75	6·22	4·72	0·18	52
16	D	1	2·06	6·35	0	High	17
17	H	0	2·37	6·74	2·91	0·56	35
18	H	0	2·38	6·83	5·08	0·15	35

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TABLE 1 (*continued*)

Case No.	Goiter		Dose retained (mc)	Uptake rate factor 10^3k_1		Sensitivity K	Follow-up time in weeks
	Type†	Size		Initial	Final		
19	D	2	2·49	7·2	3·09	0·54	49
20	D	2	3·49	7·36	1·23	1·4	20
21	D	2	*	7·80	*	0·15	24
22	R	2	1·98	7·85	3·82	0·53	50
23	N	1	*	8·02	*	0·18	31
24	R	2	*	8·2	*	0·05	52
25	D	1	2·33	8·51	6·18	0·16	27
26	N	3	*	8·66	*	0·07	21
27	D	1	2·49	8·73	3·64	0·56	24
28	D	2	*	9·17	*	0·28	22
29	D	2	2·05	9·41	3·15	0·97	52
30	N	2	*	9·63	*	0·68	36
31	N	2	*	8·01	*	0·31	34
32	D	3	8·85	11·2	4·62	0·16	47
33	D	1	3·74	11·9	4·12	0·50	48
34	N	1	3·43	12·0	3·10	0·84	35
35	N	2	9·25	12·7	5·03	0·16	8
36	D	2	*	13·2	*	0·29	26
37	D	2	*	13·6	*	0·19	31
38	D	2	*	14·4	*	0·16	9
39	N	1	3·80	15·2	2·24	1·5	21
40	D	2	*	15·2	*	0·41	23
41	H	0	*	10·0	*	0·06	22
42	D	2	3·64	15·9	2·21	1·7	23
43	D	2	3·80	16·7	3·66	0·94	50
44	N	1	3·61	18·0	8·10	0·34	9
45	D	1	4·08	20	7·58	0·40	30
46	D	2	2·18	20	50	−0·28	8
47	N	1	*	4·32	*	0·14	33
48	D	2	*	5·35	*	0·60	35
49	H	0	*	21·3	*	1·9	22
50	D	3	*	22·0	*	0·91	53
51	N	1	*	23·4	*	0·73	24
52	D	1	4·46	23·9	3·63	1·3	28
53	N	3	*	24·0	*	0·33	41
54	N	1	*	24·0	*	0·13	22
55	D	1	*	24·5	*	0·53	36
56	D	1	3·91	26·7	5·20	1·1	53
57	D	2	5·00	30	9·03	0·45	37
58	D	2	2·69	30·0	4·67	2·0	57
59	D	2	*	32·6	*	0·12	21
60	D	2	*	33·5	*	0·27	8
61	D	2	*	32·6	*	0·011	4
62	N	2	*	39·0	*	1·52	24
63	N	3	5·77	39·6	29·0	0·06	9
64	H	0	*	44·6	*	1·2	21
65	N	3	*	46·5	*	0·10	8
66	D	3	*	51·3	*	0·08	31
67	D	1	*	60	*	2·5	28
68	N	2	3·47	5·69	1·16	1·1	8
69	N	2	7·09	11·1	1·42	0·96	9
70	R	3	11·4	17·6	0·66	2·3	8

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TABLE 1 (*continued*)

Case No.	Goiter		Dose retained (mc)	Uptake rate factor $10^3 k_1$		Sensitivity K	Follow-up time in weeks
	Type†	Size		Initial	Final		
71	H	0	4·01	19·3	1·15	4·0	12
72	N	2	14·9	22·8	5·01	0·24	8
73	R	0	1·71	7·20	1·19	3·0	8
74	D	1	2·89	10·0	1·72	1·7	35
75	N	3	5·01	8·04	1·45	0·91	8
76	N	2	5·58	8·49	2·52	0·42	9
77	R	0	1·47	6·39	1·20	2·9	9
78	N	3	2·05	3·78	2·58	0·23	8
79	N	1	4·75	12·4	0·62	4·0	8
80	N	2	20·0	34·3	2·10	0·77	8
81	N	1	3·86	17·9	4·81	0·70	21
82	N	2	20·0	35·7	0·67	2·6	8
83	N	2	4·48	23·7	8·25	0·42	33
84	H	0	2·63	8·25	4·34	0·34	22
85	D	2	3·14	4·85	2·41	0·32	23
86	N	2	1·58	4·63	2·64	0·48	22
87	N	2	10·4	16·1	0·67	2·2	12
88	R	0	1·87	8·01	3·48	0·70	19
89	N	1	2·67	11·2	2·57	1·3	14
90	N	1	*	8·4	*	1·8	7
91	N	2	12·8	19·7	4·34	0·28	8

* Multiple dose cases; see also Table 2 for those with predicted response.
† D = diffuse; N = nodular; H = hyperthyroid without goiter; R = recurrent.

For the 49 predictions tabulated, the logarithm of the ratio k_1 observed/k_1 predicted has the following values:

Mean value = 0·003
Standard deviation of this mean = ±0·050
Standard deviation of individual values = ±0·349

It is evident that the mean ratio does not differ significantly from 1·0.

DISCUSSION

Study of the results provides answers to certain practical questions that arise in radio-iodine therapy.

Range of response expected from the first "test-therapy" dose

Patients, numbers A26 and 16, out of the total of 125, represent about 1·6 per cent of hypersensitive cases that would probably be classed as failures under any practicable system of dosage because unwanted myxoedema resulted from a very small dose of I^{131}.

If we exclude these two, the mean values and the standard deviations of the sensitivity factor K, calculated from Table 1, are as shown in Table 3.

In this series there is no significant difference between the mean sensitivity, K, of patients with diffuse goiters, and of those with nodular goiters; nor is there apparent any marked dependence of K on the initial level of thyroidal activity as measured by the rate factor k_1.

However, the size of the goiter has a significant influence on the mean value of K. For each size group there should be postulated a maximum K, unlikely to be exceeded in any particular patient; safe maximum

TABLE 2. Reproducibility of response in patients receiving multiple doses

Case No.	Dose (mc)	Uptake rate factor 10^3k_1		Sensitivity factor K		Predicted result 10^3k_1	Ratio $\frac{\text{actual}}{\text{predicted}}$
		Before dose	After dose	This dose	Mean		
A8	2·70	4·36	3·31	0·12			
	1·84	3·31	1·11	1·1	0·51	2·31	0·48
A11	2·59	6·72	6·66	0·003			
	3·60	6·66	6·60	0·003	0·003	6·52	1·01
	3·16	6·60	5·50	0·06	0·02	6·48	0·85
	3·03	5·50	4·06	0·12	0·05	4·83	0·84
A18	1·92	10·3	22·3	−0·28			
	2·46	22·3	4·26	1·7	0·84		
	2·48	4·26	2·81	0·21	0·61	0·82	3·43
A19	2·30	10·6	5·18	0·46			
	0·91	5·18	3·94	0·35	0·42	2·83	1·39
	1·05	3·94	2·68	0·45	0·43	2·11	1·27
A22	2·19	12·0	4·81	0·68			
	1·62	4·81	2·98	0·38	0·55	1·50	1·99
A24	3·00	14·0	8·8	0·20			
	1·75	8·8	8·0	0·06	0·14	5·21	1·54
	2·05	8·0	4·54	0·37	0·21	5·02	0·90
	1·99	4·54	1·90	0·70	0·32	2·45	0·78
A27	3·75	22·0	15·3	0·12			
	2·54	15·3	4·15	1·1	0·50	12·2	0·34
	0·93	4·15	2·81	0·51	0·50	2·16	1·30
A28	3·64	26·5	23·0	0·04			
	3·59	23·0	19·22	0·06	0·05	17·7	1·08
	3·52	19·2	11·8	0·18	0·09	14·3	0·82
11	1·88	5·69	5·44	0·02			
	3·75	5·44	4·57	0·05	0·04	4·58	1·00
21	1·72	7·80	36·4	−0·46			
	4·08	36·4	15·5	0·33	0·10		
	6·06	15·5	5·14	0·33	0·22	7·17	0·72
	2·15	5·14	9·16	−0·20	0·15	2·64	3·47
23	2·82	8·02	5·75	0·14			
	3·30	5·75	3·43	0·20	0·18	2·99	1·15
24	4·27	8·2	6·59	0·06			
	6·70	6·59	5·00	0·05	0·05	3·74	1·34
28	2·76	9·17	6·47	0·15			
	6·91	6·47	1·94	0·34	0·28	2·10	0·92
30	2·82	9·63	6·84	0·14			
	3·61	6·84	1·38	1·10	0·68	3·34	0·41
36	3·75	13·2	8·84	0·13			
	5·30	8·84	2·85	0·40	0·29	3·72	0·77
38	5·17	14·4	7·08	0·20			
	5·01	7·08	4·43	0·12	0·16	2·36	1·88
40	4·89	15·2	5·75	0·34			
	2·90	5·75	2·28	0·53	0·41	1·94	1·18
49	3·84	21·3	15·6	0·10			
	12·6	15·6	0·50	2·42	1·88	4·60	0·11
50	3·00	22·0	8·47	0·53			
	2·06	8·47	2·11	1·46	0·91	2·65	0·80
51	4·41	23·4	20·6	0·03			
	12·2	20·6	1·59	0·98	0·73	11·9	0·13
53	2·73	24·0	15·1	0·22			
	4·86	15·1	11·7	0·06	0·12	4·89	2·39
	7·35	11·7	2·32	0·55	0·33	4·32	0·54

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TABLE 2 (*continued*)

Case No.	Dose (mc)	Uptake rate factor 10^3k_1		Sensitivity factor K		Predicted result 10^3k_1	Ratio $\frac{\text{actual}}{\text{predicted}}$
		Before dose	After dose	This dose	Mean		
54	5·51	24·0	13·3	0·15			
	7·05	13·3	7·42	0·11	0·13	4·35	1·71
	10·0	7·42	3·27	0·13	0·13	2·10	1·56
55	3·68	24·5	12·6	0·26			
	7·89	12·6	2·04	0·66	0·53	2·49	0·82
59	5·21	32·6	50·2	−0·07			
	10·4	50·2	25·8	0·09	0·04		
	20·2	25·8	13·4	0·05	0·04	10·2	1·31
	24·1	13·4	1·98	0·24	0·12	4·48	0·44
60	4·53	33·5	35·4	−0·01			
	10·5	35·4	7·57	0·35	0·24		
	4·32	7·57	2·89	0·38	0·27	2·46	1·17
61	5·20	32·6	31·1	0·009			
	17·4	31·1	26·4	0·010	0·010	23·7	1·11
	39·0	26·4	22·6	0·004	0·006	14·8	1·53
	17·3	22·6	15·2	0·028	0·011	18·5	0·82
62	3·93	39·0	10·1	0·73			
	2·57	10·1	7·54	0·13	0·49	2·12	3·56
	3·07	7·54	0·61	3·7	1·5	1·87	0·33
64	6·10	44·6	5·30	1·2			
	0·82	5·30	2·98	0·95	1·2	1·77	1·68
65	6·23	46·5	22·6	0·17			
	13·0	22·6	33·6	−0·02	0·04	4·17	8·06
	32·9	33·6	6·09	0·14	0·10	9·60	0·63
66	2·71	51·3	36·4	0·15			
	4·81	36·4	27·8	0·06	0·10	14·8	1·88
	10·7	27·8	13·9	0·09	0·09	9·15	1·52
	12·9	13·9	7·24	0·07	0·08	4·06	1·78
67	2·73	60	33·4	0·29			
	4·41	33·4	13·3	0·34	0·32	9·34	1·43
	7·67	13·3	0·37	4·6	2·5	2·25	0·16

TABLE 3. Observed mean sensitivity for different groups of patients

No. of cases	Type of case	Observed sensitivity K			
		Range	Mean	S.D. of mean	Individual S.D.
123	All	−0·28 to 7·3	0·91	0·10	1·13
49	Diffuse goiters	−0·28 to 2·8	0·70	0·11	0·76
47	Nodular goiters	−0·08 to 4·0	0·73	0·12	0·80
41	Initial 10^3k_1 up to 7·2	−0·08 to 7·3	0·76	0·13	0·85
41	Initial 10^3k_1 7·2–15·2	0·05 to 4·0	0·90	0·14	0·91
41	Initial 10^3k_1 over 15·2	−0·28 to 5·7	1·07	0·19	1·22
24	Goiters size 0	0·04 to 4·0	1·26	0·22	1·10
31	Goiters size 1	0·04 to 4·0	0·96	0·17	0·92
47	Goiters size 2	−0·28 to 2·6	0·67	0·09	0·64
19	Goiters size 3 and 4	−0·08 to 2·3	0·62	0·14	0·61

values, well over 3 standard deviations above the mean values, are $K = 8$, 5 and 3 for goiter sizes 0, 1 and 2 or over, respectively. These enable the first "test-therapy" dose to be planned.

The range of sensitivity observed in different patients is very wide; so wide that if the mean K is used to predict the response to the first dose of I^{131} the actual k_1 obtained may be about 10 times greater or smaller than the predicted value.

Failure to respond to the first dose

In this series 18 patients failed to respond to a first dose, which in our cautious experimental approach, was often quite inadequate in the light of experience accumulated later. With larger repeated doses from which positive therapeutic responses have been obtained, the maximum K observed so far is 1·7 (patient A18). An arbitrary rule has been tentatively adopted, making the second "test-therapy" dose three times the first one, when the latter has failed to produce a response.

Predictability of results of repeated doses in the same patient

Larsson[16] in an extensive series, was unable to correlate the effects of repeated doses in the same patient, probably because the 24-hr uptake of I^{131} is ineffective for distinguishing moderate changes in the higher levels of thyroid function. The use of the clearance rate or k_1 is not subject to this disability, and Table 2 shows a useful degree of correlation. This is illustrated graphically in Fig. 2 for three typical cases.

As was stated earlier, the standard deviation of individual values of $\log_{10}$ (k_1 observed/k_1 predicted) is $\pm 0{\cdot}349$; from this it may be estimated that in 1 per cent of cases the observed k_1 will be lower than 1/6·48 times the predicted k_1. Similarly, in 1 per cent of all repeated doses the observed sensitivity K may be greater than 34 times the previous mean K_m.

Dosage schedule based on these experimental results

Using the experimental results discussed above, a dosage schedule has been worked out, aimed at bringing a hyperthyroid patient's uptake rate factor k_1 down to some value within the range $0{\cdot}5 \times 10^{-3}$ to 4×10^{-3};

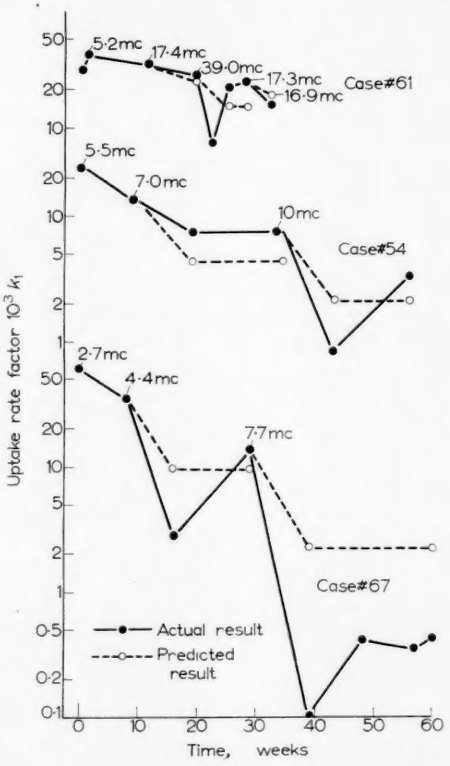

Fig. 2. Degree of predictability of response illustrated for three patients.

the lower limit is well above the rather ill-defined hypothyroid-euthyroid borderline (about $0{\cdot}23 \times 10^{-3}$) and the upper value is about the upper limit of the definitely euthyroid zone.[12] A different range may be aimed at if desired, to suit a different ecological situation.*

Clearly the first dose must be calculated to yield $k_1 = 0{\cdot}5 \times 10^{-3}$ when K has its maximum limiting value K_{max} of 8, 5 or 3,

* There is some evidence that higher k_1 levels may be applicable to Australian conditions.

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depending on the size of the goiter. Equation (2) then becomes

$$d_1 = \frac{10^3 k_a - 0{\cdot}5}{0{\cdot}5 K_{\max}} \qquad (5)$$

from which d_1 is derived for the various initial uptake rates, k_a, as in Table 4.

TABLE 4. Suggested test-therapy dosage schedule

Uptake rate $10^3 k_1$ before this dose	Dose retained d_1 (mc)		
	Gland size		
	0	1	2 or more
	Maximum sensitivity $K_{\max}$		
	8	5	3
6	1·4	2·2	3·7
7	1·6	2·6	4·3
8	1·9	3·0	5·0
9	2·1	3·4	5·7
10	2·4	3·8	6·3
12	2·9	4·6	7·7
14	3·4	5·4	9·0
16	3·9	6·2	10·3
18	4·4	7·0	11·7
20	4·9	7·8	13·0
25	6·1	9·8	16·3
30	7·4	11·8	19·7
35	8·6	13·8	20*
40	9·9	15*	20*
45	10*	15*	20*
50	10*	15*	20*

* Suggested ceiling, not according to formula.

If d_1 produces a negligible or negative response, then a new start is made with $d_2 = 3d_1$.

In the more likely event that d_1 gives a positive but insufficient response, K is calculated with d_1 in equation (2); then d_2 is found from equation (4) aimed to give a predicted $k_e' = 3{\cdot}5 \times 10^{-3}$. There is then, slightly less than 1 per cent probability that the actual k_1 will fall lower than $0{\cdot}5 \times 10^{-3}$.

Thus

$$d_2 = \frac{10^3 k_b - 3{\cdot}5}{7K} \qquad (6)$$

A similar procedure is followed for all later doses, once a definite response is obtained from a "test-therapy" dose, except that equation (3) should be used when necessary to calculate K for prediction.

The following hypothetical case illustrates the above principles.

Let the initial rate factors be $k_1 = 25 \times 10^{-3}$ and $k_2 = 2{\cdot}2 \times 10^{-3}$ for a patient with a size 1 goiter.

From Table 4 the required dose retained $d_1 = 9{\cdot}8$ mc so with equation (1) the dose administered should be

$$D = (25 + 2{\cdot}2) \times 9{\cdot}8/25 = 10{\cdot}7 \text{ mc}$$

Suppose the rate factors at follow-up are $k_1 = 13{\cdot}5 \times 10^{-3}$ and $k_2 = 2{\cdot}8 \times 10^{-3}$.

From equation (2) the observed sensitivity is

$$K = \frac{25 - 13{\cdot}5}{13{\cdot}5 \times 9{\cdot}8} = 0{\cdot}087$$

This value in equation (6) gives for the second dose retained

$$d_2 = \frac{13{\cdot}5 - 3{\cdot}5}{7 \times 0{\cdot}087} = 16{\cdot}4 \text{ mc}$$

Then with the mean k_2, the second dose administered is

$$D = (13{\cdot}5 + 2{\cdot}5) \times 16{\cdot}4/13{\cdot}5 = 19{\cdot}4 \text{ mc}$$

The above scheme is applicable for most likely cases. However, if k_1 has been brought down to $5{\cdot}6 \times 10^{-3}$ or less, and further treatment is considered desirable, the next dose should be calculated assuming that K may have its maximum value of 34 times the preceding K_m.

Thus in this case

$$d_2 = \frac{10^3 k_b - 0{\cdot}5}{17 K_m} \qquad (7)$$

Probable number of doses needed to produce a euthyroid result

With the dosage system suggested above, and the range of sensitivity shown in this series (Table 3) it is expected that a euthyroid state should be obtained with the first "test-therapy" dose in about 68 per cent of cases; each succeeding dose should have a

0·6 probability of success, so 19·2 per cent of cases would need 2 doses, 7·7 per cent 3 doses and so on. The average number of doses works out as 1·5 with a probable incidence of 0·53 per cent of hypothyroid results; to this must be added 1·6 per cent more hypothyroid cases because of the two hypersensitive cases excluded from this analysis. The expected total incidence of 2·1 per cent may be compared with the 15 per cent reported by Beierwaltes *et al.*,[19] using an average of 1·3 doses per patient.

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Isotope Transfer Test in the Diagnosis and Treatment of Hydrocephalus*

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(*Received* 11 *September* 1958)

A technique is described in which 100 μc of radioactive (I^{131}) serum albumin is injected into the cerebral ventricles following which characteristic graphs of radioactivity are constructed to denote ventriculo subarachnoidal block. The method has been used in 30 cases and has been helpful in delineating blocks in the cerebrospinal fluid pathways at the level of the Aqueduct of Sylvius and the portals of exit at the fourth ventricle. In ten patients ventriculo-peritoneal shunts were performed. Nine of the shunting tubes became blocked at variable intervals after operation. Three of the patients with blocked shunts were noted to have no progressive enlargement of the head after a period of 1 year and were considered arrested despite measurements indicating a blocked tube.

This same procedure has been used in the diagnosis of hydrocephalus *ex vacuo* and has been instrumental in the reduction of morbidity and mortality associated with exploration of the posterior cranial fossa. Only one minor episode of hyperpyrexia was attributed to the test itself.

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ÉPREUVE DU TRANSFERT ISOTOPIQUE DANS LE DIAGNOSTIC ET LE TRAITEMENT DE L'HYDROCÉPHALIE

Une technique est ici décrite qui consiste à injecter 100 μc d'albumine serique radioactive (I^{131}) dans les ventricules cérébraux, après quoi des graphiques caracterisant la radioactivité sont construits afin de déceler un bloc sousarachnoidien. La méthode a été utilisée dans 30 cas et s'est avérée utile dans la localisation des bloquages du courant du Liquide Céphalo-Rachidien au niveau de L'Aqueduct de Sylvius et des issues de sortie du IV^{e} ventricule. Chez 10 patients des "shunts" ventriculo-peritonéaux ont été pratiqués. Neuf des 10 tubes-shunts se sont bloqués à des périodes variables après l'operation. Trois des malades où ces anastomoses se sont bloquées n'ont pas montré après une année d'observation une augmentation progressive du périmètre céphalique et étaient considerés cliniquement stables malgré le fait que nos méthodes ont démontré un bloc.

Cette même technique a été utilisée pour le diagnostic de l'hydrocéphalie *ex vacuo* et s'est avérée d'une grande aide dans la réduction de la mortalité et morbidité associées avec l'exploration de la fosse postérieure du crâne. Seul un episode d'hyperpyrexie moderée a été attribué directement au test lui-même.

ИСПЫТАНИЕ ПЕРЕДАТОЧНОГО ИЗОТОПА В ДИАГНОЗЕ И ОБРАБОТКЕ ГИДРОСЕФАЛИТА

Описание способа, где 100 микрограм I^{131} (радиоактивный серум альбумин) впрыскивается в полость желудочков головного мозга. Вслед за этим характерые кривые радиоактивности построены для демонстрации блока между желудочками и субарочнодальным пространством.

* Presented at Fifth Annual Meeting of The Society of Nuclear Medicine June 19–21, 1958, at Los Angeles, California.

Этот способ был употреблен в 30 случаях и позволил определить препятствие в циркуляции спинномозговой жидкости на уровне Aqueduct of Sylvius и выходов из четвертого желудочка.

В 10 случаях было осуществлено сообщение между желудочками и брюшной полостью употребляя Poliethylen Catheter.

В 9 случаях catheter через различные промежутки времени закупорился.

В 3 случаях где catheter был закупорен авторы не наблюдали увеличения окружности черепа больше года после операции. Hydrocephalus не прогрессировал несмотря на закупорку. Этот же способ был употреблен для диагноза hydrocephalus *ex vacuo* и позволил значительно снизить смертность и осложнения связанные с операциями в области posterior cranial fossa.

Осложнение в связи с описанным способом наблюдалось только в одном случае —подъем температуры до 39° на несколько часов.

ISOTOPENTRANSPORT-TEST IN DIAGNOSE UND THERAPIE VON HYDROCEPHALUS

Eine Methode ist beschrieben in der 100 μc radioaktiven (I^{131}) Serum Albumens in die cerebralen Ventrikel injiziert werden. Charakteristische Kurven koennen daraufhin konstruiert werden zur Darstellung ventrikulaerer subarachnoidaler Verschluesse. Diese Methode wurde in 30 Faellen angewandt und hat sich als hilfreich in der Darstellung der Blockierung der cerebrospinalen Fluessigkeit in der Hoehe des Aquaeducuts Sylvii und der Austritts Oeffnung im vierten Ventrikel erwiesen. Ventriculo-peritoneale Umleitungen wurden in 10 Patienten durchgefuehrt. Neun der Umleitungen blockierten in verschieden Zwischenraeumen nach der Operation. Nach einem Zwischenraum von einem Jahr war keine fortschreitende Vergroesserung des Kopfes in drei Patienten festzustellen. Diese Faelle wurden als arrestiert angesehen, ebwohl radioaktive Messungen eine Blockierung der Umleitung anzeigten.

Dieselbe Methode wurde in der Diagnose des Hydrocephalus *ex vacuo* angewandt und hat sich als instrumentell in der Reduktion der Morbiditaet und Mortalitaet in Verbindung mit der Exploration der fossa cran. post. erwiesen. Nur eine unbedeutende Episode von Hyperpyrexia wurde auf den Test zurueckgefuehrt.

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INTRODUCTION

Hydrocephalus, or the excessive accumulation of cerebro-spinal fluid within the cranium, has many difficulties in classification. The accepted nomenclature seems to be confused with descriptive terms having little reference to the entity producing the clinical syndrome. Despite these confusing terms all varieties of hydrocephalus have one thing in common; namely, an obstruction to the flow of cerebrospinal fluid. The obstructive process may have origin in a congenital malformation, inflammatory process, be secondary to cerebral trauma, or in association with tumor. The anatomical sites for these lesions are best illustrated (Fig. 1). The common sites for obstruction are: (A) the foramen of Monro; (B) the third ventricle; (C) the iter; (D) the fourth ventricle and its outlets through the foraminae of Luschka and Magendie; (E) the cerebral subarachnoidal space; and (F) the

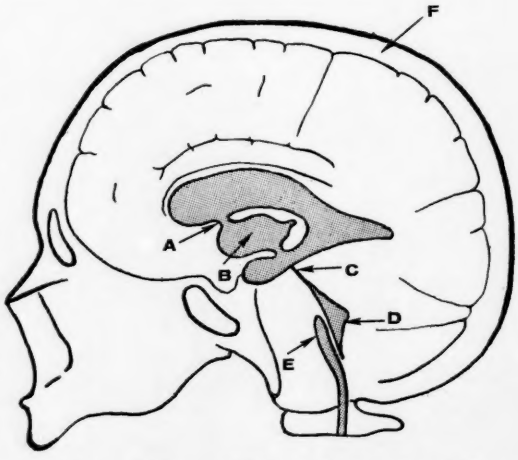

Fig. 1. A diagram of the principal pathways for cerebrospinal fluid. (A) The foramen of Monro, (B) the third ventricle, (C) the iter, (D) the fourth ventricle and (E) the cerebral subarachnoidal space. Site (F) is the region of the major venous sinuses.

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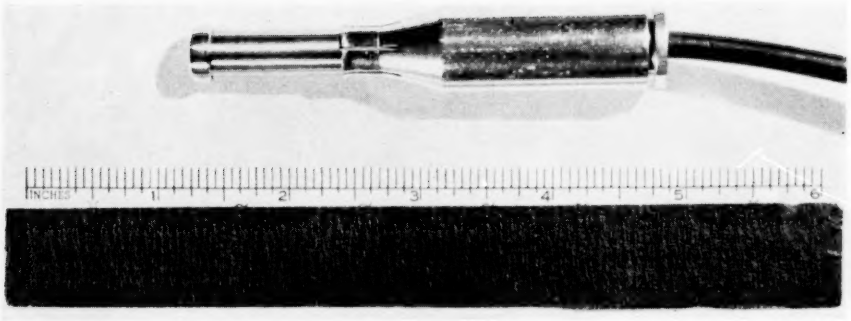

FIG. 2. A typical G–M eye probe: operating voltage 750.

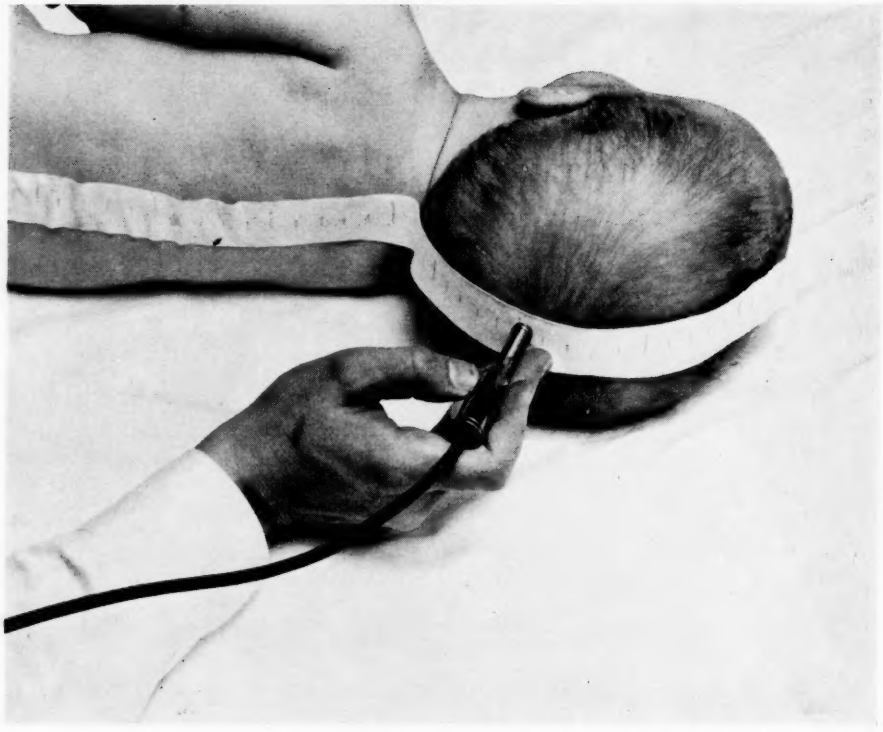

FIG. 3. Measurements being made along a saggital plane of the head and spine.

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venous sinuses of the dura mater. The test to be described has been found most useful in the diagnosis of block between the outlet of the fourth ventricle and the cerebral subarachnoidal space at site (D).

For some time we have been interested in the rate of exchange of RISA (radio-iodinated serum albumin) between the cerebrospinal fluid and the peripheral circulation. It soon became apparent that RISA was an innocuous substance that would remain as a slug of highly mobile material which upon manipulation of the head produces a flow through the ventricular system. Here then was a method to measure the patency of the ventricular system.

METHOD

Radio-iodinated human serum was used in all of the patients. Infants needed no burr holes to reach the lateral ventricles because the fontanels were patent. In the case of adults the material was introduced through a previously made cranial burr hole. The dosage was 100 μc. Immediately following instillation, the patient was placed upright for several minutes. Counts were obtained with a G–M eye probe (Fig. 2) beginning at the anterior fontanel and continuing along the saggital plane of the head and spine (Fig. 3). Counts were taken for 1 min and plotted versus the inverse square of the distance from the starting point. In the case of obstruction at the level of the fourth ventricle and the outflow apertures to the subarachnoidal space, a straight line graph resulted when the counts per minute were plotted versus the inverse square of the distance. However, when free communication exists, the law of inverse squares does not hold and the intensity of radiation along the cerebrospinal axis becomes directly proportional to the cross-sectional area of the spinal subarachnoidal space under observation, the rate of diffusion of the tracer material, and possibly the pumping action of the choroid plexus.

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RESULTS

Thirty patients with clinical evidence of hydrocephalus were submitted to the isotope transfer test. Only one patient exhibited a mild episode of hyperpyrexia which lasted 48 hr and responded to symptomatic therapy. The following case histories are illustrative.

Case 2. KCH 101055. L. G., a 3-month-old female, was admitted to the hospital because of drowsiness, poor feeding habits, and increasing size of the head. At one month of age a lumbar meningocele had been surgically closed at another hospital. On entry, the circumference of the head was 60 cm at the occipitobregmatic level. The circumference of the chest was 42 cm. A ventricular tap was performed through a patent anterior fontanel. The ventricular fluid was moderately turbid and contained large numbers of polymorphonuclear leukocytes. One hundred μc of RISA were injected into the right lateral ventricle and counting performed as described. The results were plotted (Fig. 4). The patient died 1 week later despite vigorous treatment for ventriculitis and meningitis. Postmortem examination disclosed an intense ventriculitis, adhesive arachnoiditis which blocked the foraminae

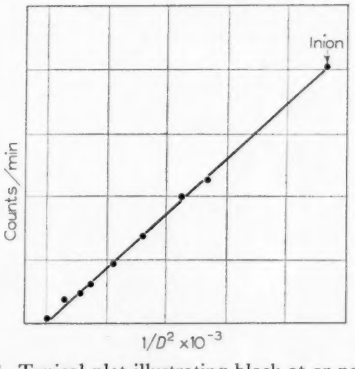

FIG. 4. Typical plot illustrating block at or near the fourth ventricle. C.P.M. (counts/min), $1/D^2$ (distance from the point of injection).

of Magendie and Luschka, basilar meningitis, and a meningitis throughout the spinal subarachnoidal space.

Comment: Fig. 4 represents a typical plot of isotope transfer in an example of ventriculosubarachnoidal block.

Case 28. KCH 131223. B. J., a 17-day-old female, was admitted to the hospital for diagnosis and treatment of a mass protruding from the skull. Examination disclosed a meningocele protruding from the midline occipital area. The mass was surgically excised and a plastic repair of the scalp was effected. The circumference of the head increased from 39 cm to 42 cm in the next 4 days. The fontanels became tense, the infant fed poorly, and became less responsive to noxious stimuli. An isotope transfer test was performed which showed block of the cerebrospinal fluid in a position similar to that already noted in Case 2. A ventriculoperitoneostomy was performed with almost immediate evidence of ventricular decompression. The patient gradually became more alert, feeding habits improved, and head circumference decreased to 38 cm. An isotope transfer test was performed and the radiation flux was measured along the cerebrospinal axis (Fig. 5). Measurements were then made over the shunting tube and plotted as shown in Fig. 6.

Comment: Fig. 5 is a typical plot observed in instances of block of the ventricular pathway. The complex curve measured from readings obtained over the course of the shunt illustrates how it is possible to determine the patency of the tube (Fig. 6).[1]

Case 19. KCH 111632. J. B., a 74-year-old male, was admitted for treatment of dizziness, headaches, and progressive drowsiness. Neurological examination was negative except for brisk reflexes in all four extremities, and the presence of bilateral signs of Babinski. A ventriculogram disclosed mild dilitation of the cerebral ventricles. The ventricular fluid was slightly xanthrochromic. The fourth ventricle was not visualized. One hundred μc of RISA were injected into the right lateral ventricle. Measurements were carried out as described. The data were plotted (Fig. 7).

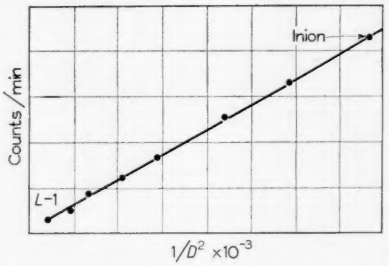

FIG. 5. Graph showing block between the ventricles and the subarachnoidal space.

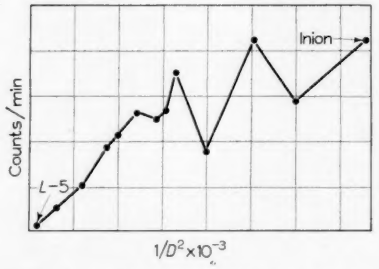

FIG. 6. This graph shows that the shunt tube is patent.

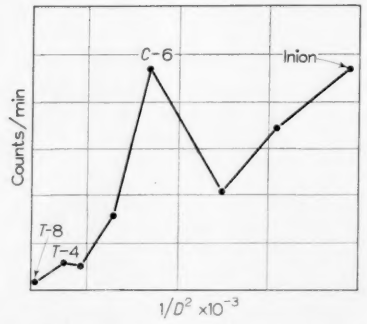

FIG. 7. This complex curve demonstrates there is no block of the radioactive material in a case of "hydrocephalus, *ex vacuo*."

Comment: Fig. 7 represents a complex curve illustrating patency of the ventriculosubarachnoidal pathways. The patient subsequently died, and at autopsy a basilar artery thrombosis accompanied by pontine and cerebellar softening was found. The loss of cerebral substance was attributed to cerebral atrophy producing "hydrocephalus *ex vacuo*."

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DISCUSSION

Thirty cases of hydrocephalus were studied. They were almost evenly divided between patients exhibiting block between the cerebral ventricles and the subarachnoidal space and those manifesting no block in this position. Ventriculo-peritoneal shunts had been performed on ten patients. Nine of the shunting tubes became blocked at various intervals following operation. Three of the patients with block of the shunting tube did not have progressive head enlargement after one year and were presumed to have arrested hydrocephalus in spite of a negative isotope transfer test suggesting a block of the tube. In one case there was a block at the level of the posterior part of the third ventricle as demonstated by the test, and at autopsy there was a block of the rostral end of the iter by an astrocytoma. A block rostral to the fourth ventricle can be suspected when the law of radiation holds proximal to the inion.

SUMMARY

The use of the isotope transfer test as herein described is the simplest and safest method for determining either patency or block of the foraminae of exit of the cerebrospinal fluid from the fourth ventricle. Limited experience thus far suggests that obstruction at the level of the iter may be differentiated from blockage of the foraminae of Luschka and Magendie. In addition, the test is useful in determining the patency of shunting tubes *in situ*.

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Autoradiographic Localization of P^{32} Phosphate in Metastatic Carcinoma of the Breast to Bone*

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(*Received* 18 *September* 1958)

The use of P^{32}-labeled phosphate as palliative therapy in carcinoma of the breast, metastatic to bone, has had widespread trial. Clinical observation has suggested that relief of symptoms from the metastatic tumors occurs principally in bone lesions. To confirm the site of P^{32} localization, sections of human bone containing lesions recently treated with P^{32} were examined autoradiographically. Phosphorus^{32} activity as determined by this technique and microscopic localization of radionecrosis was confined to the periphery of the lesions. X-ray shadowgraphs confirmed this observation, the areas of P^{32} concentration coinciding with areas of new bone trabeculae. Gross examination showed hemorrhagic changes in the bone at the sites described. The tumor tissue showed little gross change. Serial determination of alkaline phosphatase activity in the patient shows a marked sensitivity to P^{32} therapy and appears to be a better criterion than the white blood count for controlling dosage.

Preliminary conclusions from these observations would suggest that P^{32} phosphate therapy of metastatic carcinoma of the breast to bone is dependent upon localization in regenerating bone surrounding the lesion. Therapeutic effect may be produced by decreasing the intraosseous pressure of regenerating bone, and may secondarily affect the lesion by surrounding it with a shell of radioactivity.

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LOCALISATION AUTORADIOGRAPHIQUE DU PHOSPHATE À P^{32} DANS LE CARCINOME MÉTASTATIQUE DU SEIN À L'OS

L'emploi du phosphate marqué au P^{32} a été largement essayé comme thérapie palliative pour le carcinome du sein, métastatique à l'os. Les observations cliniques ont indiqué que le soulagement des symptômes des tumeurs métastatiques s'achève principalement dans les lésions osseuses. Pour rendre certain l'emplacement de localisation du P^{32}, des sections d'os humain contenant des lésions traitées récemment avec du P^{32} furent examinées à l'autoradiographie. L'activité du P^{32}, observée par cette méthode, ainsi que la localisation microscopique de la radionécrosie, fut limitée à la périphérie des lésions. Des photographies aux rayons X accordèrent à cette observation, les régions de concentration de P^{32} étant les régions de trabécules de nouvel os. L'examen grossier indiqua des changements hémorrhagiques dans l'os aux endroits décrits. Le tissu de la tumeur montra peu de changement grossier. Le dosage en série de l'activité de phosphatase alcaline dans le malade montre une sensibilité évidente à la thérapie au P^{32} et semble un meilleur critère que le comptage des cellules blanches du sang pour contrôler le dosage.

Les premières conclusions de ses observations indiqueraient que la thérapie à phosphate-P^{32} du carcinome métastatique du sein à l'os dépend de la localisation dans le nouvel os qui se forme autour de la lésion. L'effet thérapeutique peut se produire en diminuant la pression intraosseuse de l'os nouveau-formé, et peut de façon secondaire influencer la lésion en l'entourant d'une "écale" radioactive.

* This paper was read before the Society of Nuclear Medicine at Los Angeles, California on 20 June 1958.

РАДИОАУТОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ ЛОКАЛИЗАЦИИ P^{32} В КОСТНЫХ МЕТЕСТАЗАХ КАРЦИНОМЫ ГРУДНОЙ ЖЕЛЕЗЫ

Прменение P^{32} для паллиативной терапии костных метастазов карциномы грудной железы испытывалось неоднократно. На основании клинических наблюдений предполагалось, что облегчение симптомов при костных метастазах обусловлено главным образом состоянием именно в пораженных участках костей. Чтобы подтвердить накопление P^{32} в соответствующих участках, было проведено радиоаутографическое исследование костных срезов в области метастазов у больных, которым незадолго до исследования была введена терапевтическая доза P^{32}. Этим методом было обнаружено, что радиофосфор накапливается преимущественно на периферии пораженного участка, что совпадает с областью микроскопически обнаруживаемых радионекрозов. Подобные наблюдения подтверждаются также и с помощью теневой рентгенографии: области повышенной концентрации P^{32} совпадают с областью образования новых костных трабекул. Макроскопическое исследование выявляет наличие геморрагических изменений в тех же областях костной ткани, тогда как в ткани самой опухоли макроскопические изменения незначительны. Щелочная фосфатазная активность (при обследовании больных в динамике) оказалась довольно чувствительной к лучевому воздействию P^{32}. При определении терапевтической дозы P^{32} лучше, по-видимому, руководствоваться этим показателем, а не лейкоцитарной формулой.

На основании предварительных выводов из этих наблюдений можно предполагать, что результат радиофосфатной терапии костных метастазов карциномы грудной железы зависит от локализации P^{32} в регенерирующей костной ткани, окружающей область метастаза. Терапевтический эффект может быть вызван уменьшением внутрикостного напряжения регенерирующей ткани и, кроме того, лучевым воздействием на опухоль со стороны окружающей её радиоактивной оболочки.

AUTORADIOGRAPHISCHE LOKALISIERUNG VON P-32-HÄLTIGEM PHOSPHAT IN METASTASEN VON MAMAKARZINOM IN DEN KNOCHEN

Die Verwendung von P-32-markiertem Phosphat als Palliativtherapie bei im Knochen metastasierendem Mamakarzinom wurde weitverbreitet versucht. Klinische Beobachtung zeigt an, dass eine Erleichterung der Symptome von Tumormetastasen hauptsächlich bei Knochenverletzungen auftritt. Um die örtliche Fixierung von P-32 zu bestätigen, wurden Schnitte von erkrankten mensihlichen Knochen, die kurz zuvor mit P-32 behandelt worden waren, autoradiographisch untersucht. P-32-Aktivität, die mit Hilfe dieser Technik nachgewiesen wurde, und mikroskopische Lokalisierung von Radionekrose wurde an der Peripherie der erkrankten Gebiete festgestellt. Röntgenschattenbilder bestätigten diese Beobachtung: Die Gebiete der P-32-Konzentrierung entsprachen denen der Trabeculae frischer Knochen. Grobe Untersuchungen zeigten hämorrhagiaartige Veränderungen im Knochen an den beschriebenen Stellen. Das Tumorgewebe zeigte wenig starke Veränderungen. Serienmässige Bestimmungen der Aktivität der alkalischen Phosphatase in den Patienten zeigt ein deutliches Ansprechen auf die P-32-Therapie und scheint ein besseres Kriterium für die Dosiskontrolle zu sein, als die Zählung der weissen Blutkörperchen.

Vorläufige Schlüsse aus diesen Beobachtungen weisen darauf hin, dass die P-32-Phosphattherapie der Knochenmetastasen des Brustkarzinoms auf der Fixierung in dem das geschädigte Gebiet umgebenden regenerierenden Knochen abhängig ist. Die therapeutische Wirkung könnte durch Abnahme des intraossalen Druckes im regenerierenden Knochen bewirkt werden und könnte ausserdem dadurch die Erkrankung bekämpfen, da diese von einer radioaktiven Zone umschlossen wird.

THE use of P^{32}-labeled phosphate as palliative therapy in carcinoma of the breast, metastatic to bone, was initially reported by FRIEDELL and STORAASLI.[1] Concomitant treatment with testosterone is used in the therapeutic regimen described by MAXFIELD *et al.*[2] and has had widespread clinical trial. Clinical observations suggest that relief of symptoms from the metastatic tumors occurs principally in bone lesions. Consequently this type of therapy is indicated in such cases not amenable to X-ray therapy because of generalized distribution. Therapy with P^{32} to prevent operative spread of breast carcinoma has been reported by LOW-BEER and BELL.[4,5]

Localization of P^{32} phosphate in bone as compared to other tissues has shown a marked differential concentration in bone in the normal.[3] It would appear desirable to study in more detail the site of localization of P^{32} phosphate in metastatic lesions to the bone from carcinoma of the breast than has been previously accomplished.[1,2] Autopsy specimens of bone from a patient with widespread breast carcinomatosis undergoing P^{32} testerone therapy were obtained. Using autoradiographic techniques, distribution of P^{32} activity was noted in bone, metastatic tumor to bone, in bone surrounding the lesions and in some adjacent soft tissue.

METHOD

The bone sections studied were obtained at autopsy; the most active specimens, (the vertebrae), contained sufficient P^{32} activity to read over 20 mr/hr on contact when measured with a portable G–M counter.* The bones and attached soft tissue were frozen while fresh. The frozen specimens were embedded in plaster of Paris and the entire block refrozen. The block was sectioned with a band saw in 0·5 cm thicknesses and prevented from thawing by storing on dry ice. The cut surface was cleared of plaster and tissue debris by scraping the surface with the sharp edge of a glass slide. The sections were wrapped in "Pliofilm" and placed upon unexposed X-ray film in a cassette. During exposure for 18 hr, the cassette was stored in a deep freeze. In addition to the autoradiograph, radiographs and photographs of the sections were obtained. Serial determination of white blood count and serum alkaline phosphatase (modified Bodansky method) levels were obtained in the patients studied.

RESULTS

The site of P^{32} phosphate distribution is apparent in Figs. 1 and 2. Soft tissue showed minimal concentration of P^{32}. The least concentration was observed in the fibrocartilage of the intervertebral discs. The concentration in muscle and tumor metastasis in bone appeared equal. Concentration in cortical bone was slightly greater than soft tissue. Cancellous bone and bone adjacent to tumor metastasis showed the maximum P^{32} activity. The most active concentration of P^{32} in bone was associated with hemorrhagic change in the bone with some hemorrhage into the adjacent tumor metastasis.

Microscopic sections of undecalcified vertebral bone containing extensive metastasis show replacement by tumor cells in the radiolucent areas of minimal P^{32} concentration (Figs. 3, 4, 5). The larger replaced areas show cells with well-stained and defined nuclei and minimal radiation damage. The intermediate-sized replaced areas show viable cells in the center of the radiolucent areas and a rim of eosinophilic, acellular material adjacent to the bone spicules. Smaller areas

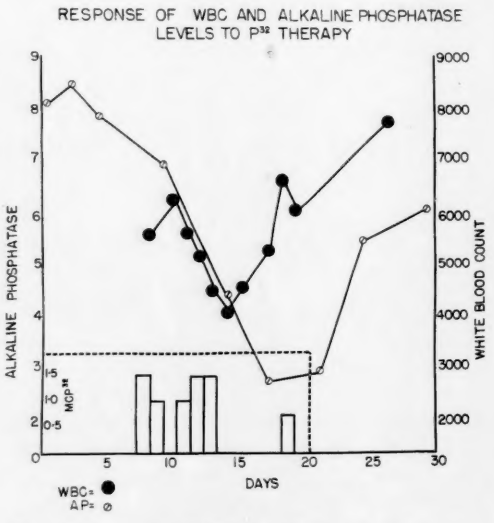

FIG. 6. Response of WBC and alkaline phosphatase levels to therapy. W^{32}

* Model 263M, Victoreen Instrument Company.

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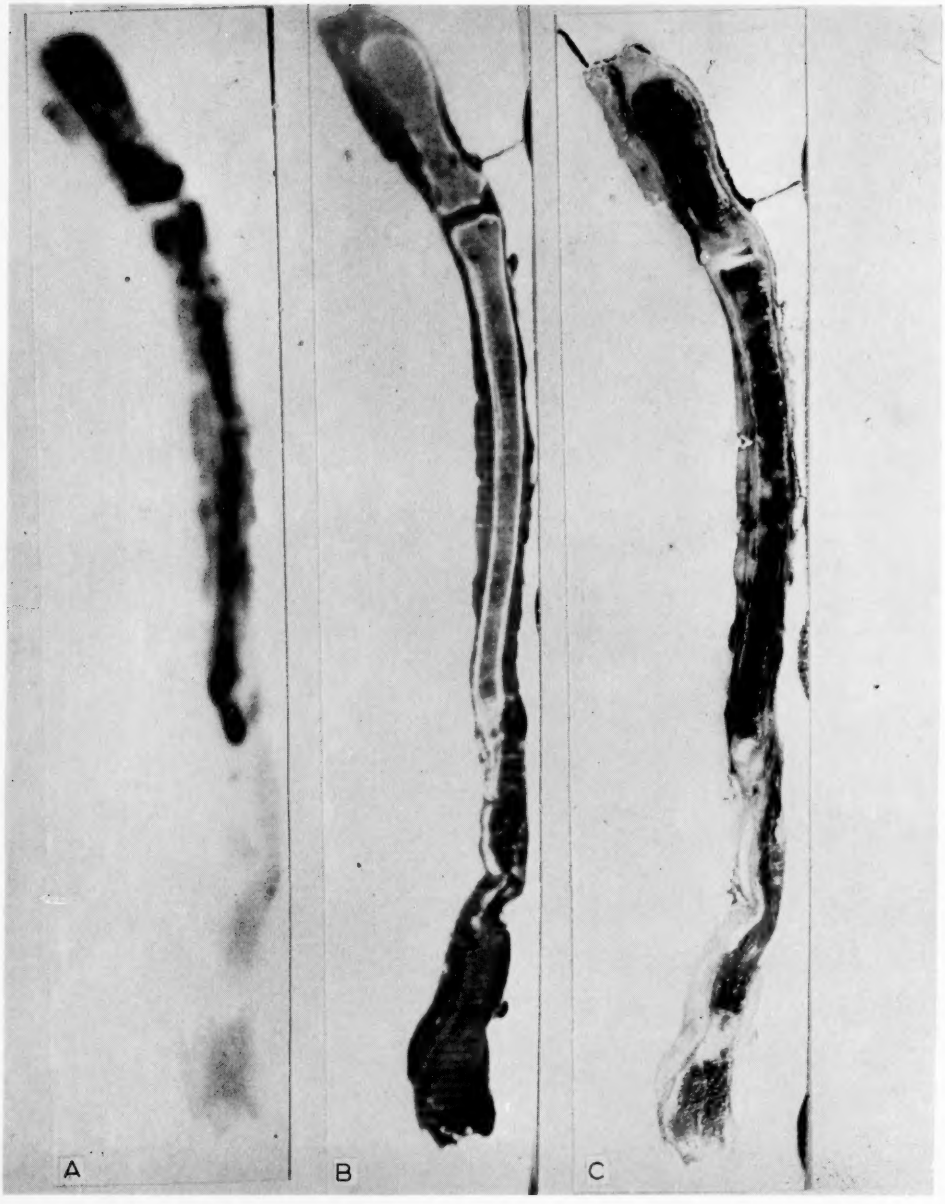

FIG. 1. Section through human sternum with some involvement by metastatic carcinoma of the breast. A. Autoradiograph of P^{32} distribution. Note the minimal concentration of P^{32} in the surrounding soft tissue and the dense bone. B. Radiograph. C. Photograph.

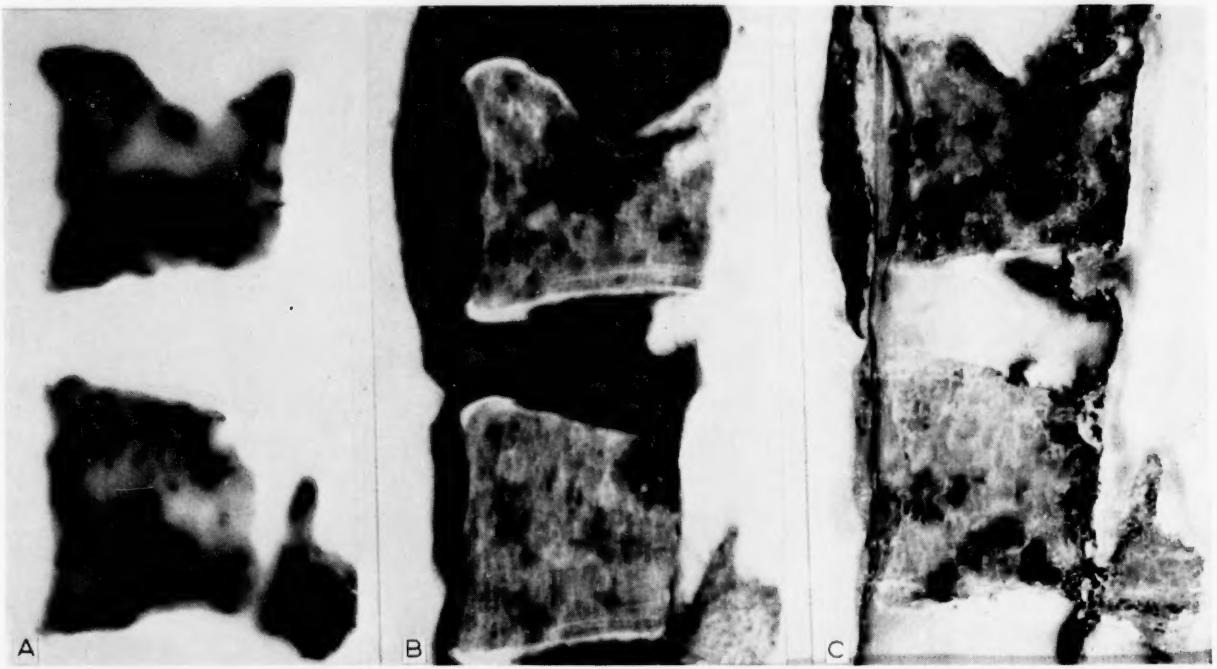

FIG. 2. Typical section through human vertebrae with massive metastatic involvement by carcinoma of the breast. After P^{32} therapy.

A. Autoradiograph. Note the minimal concentration of P^{32} activity in areas that are radiolucent in the radiograph (B).

B. Radiograph. The radiolucent areas on microscopic section show tumor cells. (See Fig. 3B.)

C. Photograph. The intervertebral discs show a complete lack of P^{32} concentration in autoradiograph (A).

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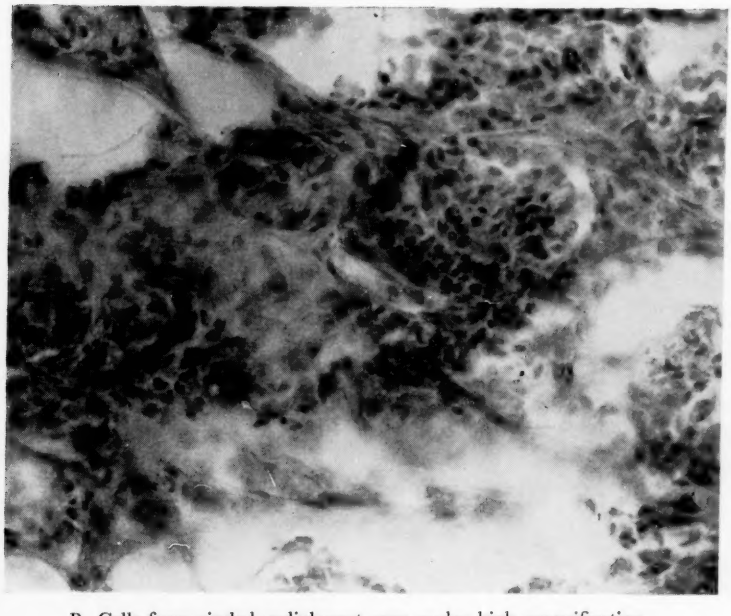
A. The upper circle concentrates little P^{32} and shows many viable tumor cells. The rectangle to the right reveals central viability of tumor cells with peripheral acellularity. The rectangle to the left and several comparable areas of marked P^{32} concentration show nearly complete acellularity.



B. Cells from circled radiolucent area under high magnification. Radiation damage is minimal.

FIG. 3. Histological section through vertebrae shown grossly in Fig. 2.

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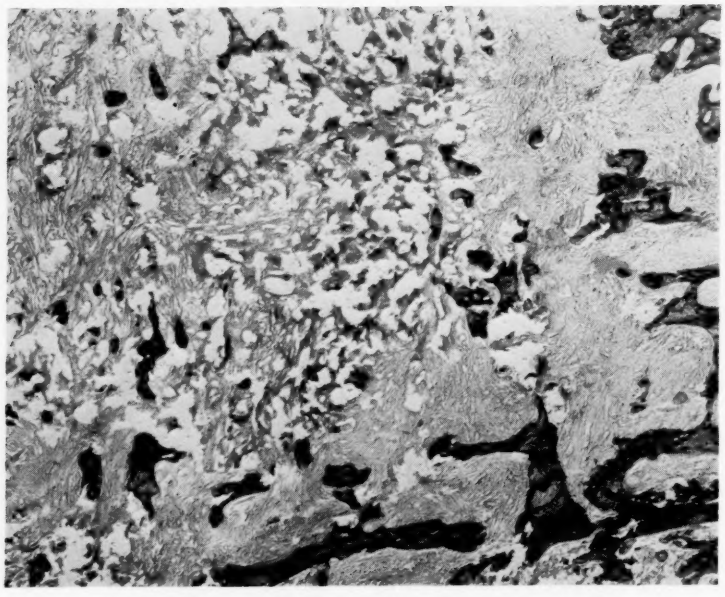
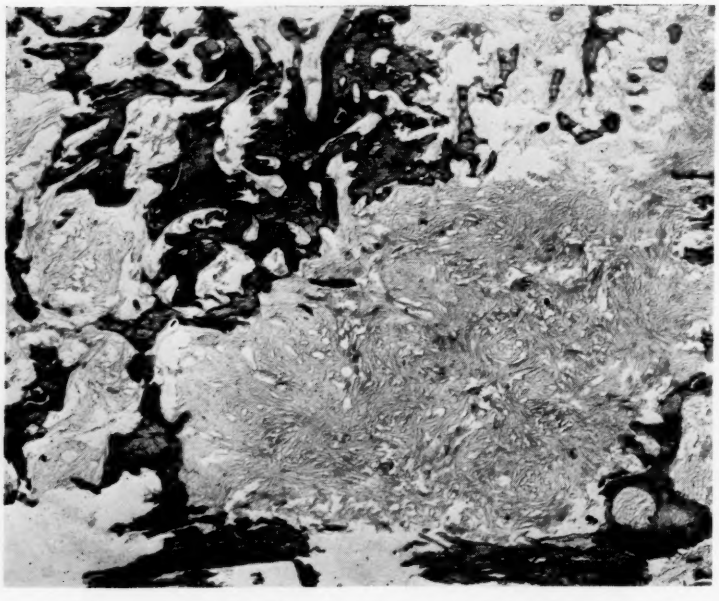


A. Area (Fig. 3A right rectangle) showing radionecrosis extending out about 1 mm from bone spicules. Central area contains viable tumor cells.



B. Area (Fig. 3A left rectangle) surrounded by bone spicules. Note the widespread radiation damage with few nuclei remaining.

FIG. 4.

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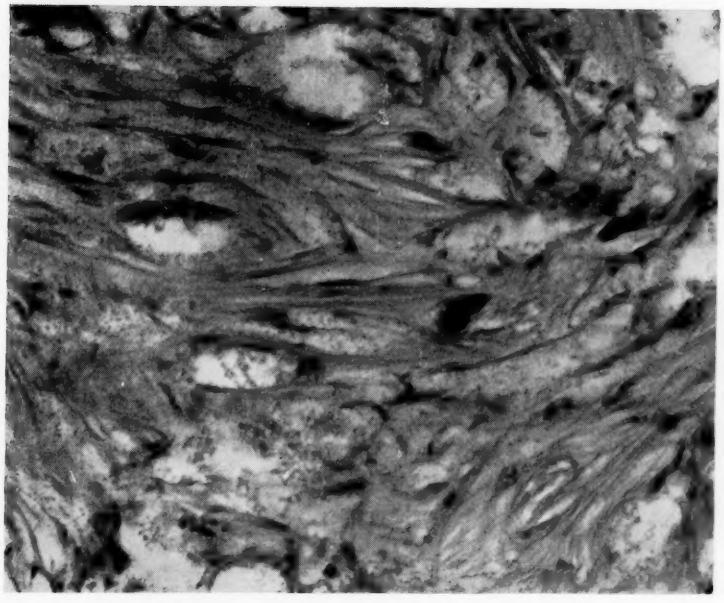
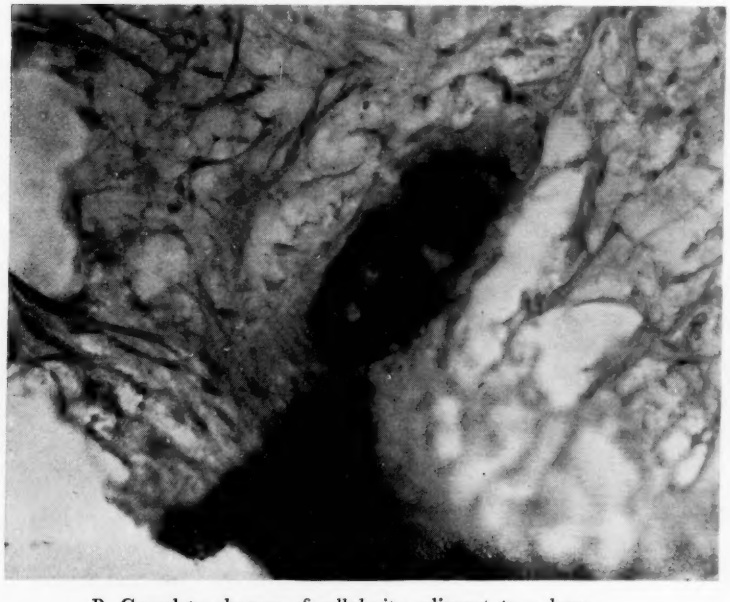


A. High power (Fig. 4B) showing only a few picnotic nuclei and extensive eosinophilic material.



B. Complete absence of cellularity adjacent to a bone spicule which is partially mineralized.

FIG. 5.

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surrounded by bone trabeculae show complete replacement by acellular, apparently non-viable material containing occasional picnotic nuclei. Serial serum alkaline phosphatase values when initially elevated show a marked reduction in response to therapy with P^{32}, and rebound rapidly with a cessation of therapy (Fig. 6). When therapy is given at daily intervals the leukocyte count also drops. The WBC decline is not as marked as the fall in elevated alkaline phosphatase values and recovers more rapidly. When P^{32} therapy is given at less frequent intervals, the elevated phosphatase values drop with each dose and recover rapidly while the depression of WBC is decreased. At such time as the phosphatase values approach normal levels, the WBC is more readily depressed by additional P^{32}.

DISCUSSION

Localization of P^{32} activity in metastatic tumor tissue was minimal and is probably insufficient by itself to produce the reported clinical improvement. The maximum concentration of P^{32} was noted in areas adjacent to metastatic lesions and in areas of regenerating bone trabeculae as suggested by microscopic examination and the radiographs. Further support for this localization is furnished by the fall in the elevated alkaline phosphatase values. Osteoblastic activity in regenerating bone is the probable principal source of these elevated values; phosphate deposition is proportional to alkaline phosphatase values,[6,7,8] thus producing an intense local irradiation from incorporated P^{32}. In order to assure localization in bone metastasis it would be well to rule out elevation of alkaline phosphatase which may result from hepatic metastasis. It would appear that osteoblastic activity would protect the bone marrow by channeling the phosphate from myeloid precursors to regenerating bone, the alkaline phosphatase level thus being a more sensitive and more appropriate criterion for titrating dosage than the white blood count.

The reported observations which unquestionably need further confirmation would not rule out therapeutic benefit but may rather explain relief from bone pain as resulting from decrease of intraosseous pressure initially produced by rapid growth of regenerating bone and tumor tissue. A secondary effect upon the metastatic lesions in bone would come from irradiation of the periphery of the tumor by beta emission from the surrounding shell of new bone. The hemorrhagic changes may well lead to compromise of the vascular supply to the lesion.

Preliminary conclusions from the data and the above postulates would suggest a more rational approach to the treatment of metastatic carcinoma of breast to bone with P^{32} phosphate. The indications for such therapy being metastatic bone involvement with elevated alkaline phosphatase levels and bone pain; protection against adverse side effects indicated by observing serially not only the WBC, but the alkaline phosphatase values and stopping dosage of P^{32} when the latter values approach normal.

SUMMARY

(1) The localization of P^{32} phosphate was determined in metastatic carcinoma of the breast to bone.

(2) The relationship of this localization to alkaline phosphatase values is discussed as applied to rationale for therapy and control of dosage.

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Gammaspectrometry for Analysis of Mixtures of Radioisotopes in Biological and Medical Research*

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With a single channel pulse height analyser it has been possible to determine radioactive nuclides in mixtures even with very low activities. The amounts of each nuclide present have been calculated from the counting rates observed in fixed energy channels. This procedure is very simple and accurate provided pulse height amplification is extremely stable. It was again confirmed that a photomultiplier tube containing silver-magnesium dynodes cannot be used for accurate work of this kind. An RCA tube 6655 gave good results. Applications on mixtures of Cr^{51}–I^{131} and Na^{24}–K^{42} are described.

LA GAMMASPECTROMÉTRIE POUR L'ANALYSE DES MÉLANGES DE RADIOISOTOPES DANS LES RECHERCHES BIOLOGIQUES ET MEDICALES

Avec un analysateur de hauteur d'impulsions à cannelation unique on a trouvé possible la détermination des nucléides radioactifs dans les mélanges même aux activités très basses. La quantité de chaque nucléide présent a été calculé des taux de compte observés aux canaux à énergie fixe. Ce procédé est très simple et précis pourvu que l'amplification de la hauteur d'impulsion soit extrèmement stable. On a affirmé de nouveau qu'un tube photomultiplicateur contenant des dynodes d'argent-magnésium ne peut point servir pour du travail exact de ce genre. Une lampe RCA 6655 donna de bons résultats. Des applications sur des mélanges de Cr^{151}–I^{131} et de Na^{24}–K^{42} sont décrites.

ИСПОЛЬЗОВАНИЕ ГАММАСПЕКТРОМЕТРИИ ДЛЯ АНАЛИЗА РАДИОИЗОТОПНЫХ СМЕСЕЙ В БИОЛОГИЧЕСКИХ И МЕДИЦИНСКИХ ИССЛЕДОВАНИЯХ

Одноканальный амплитудный анализатор импульсов дает возможность определять радиоактивные изотопы в смесях очень низкой активности. Количество каждого изотопа определялось по скорости отсчета в определенных энергетических каналах. При условии большой стабильности усиления импульсов методика оказывается очень простой и точной. Получено повторное подтверждение того, что фотоумножитель, содержащий серебряно-магнезиевые диноды не дает необходимой точности. Хорошие результаты дала трубка PCA 6655. Описано применение данного прибора при работе со смесями Cr^{51}–I^{131} и Na^{24}–K^{42}.

GAMMASPEKTROMETRIE FÜR DIE ANALYSE VON RADIOISOTOPEN-GEMISCHEN IN BIOLOGISCHER UND MEDIZINISCHER FORSCHUNG

Mit einem Ein-Kanal-Impulshöhendiskriminator war es möglich Radionukleide auch in Mischungen von sehr geringer Aktivität zu bestimmen. Die Menge der vorhandenen Nukleide wurde aus der Zählrate, die bei feststehenden Energiekanälen beobachtet wurden, errechnet. Dieses Verfahren ist sehr einfach und auch genau, vorausgesetzt, dass die Impulshöhenverstärkung ideal konstant ist. Es wurde aufs Neue festgestellt, dass Photovervielfacherröhren die

* This investigation was supported by "Knut och Alice Wallenbergs Stiftelse".

Silber-Magnesium-Dyoden enthalten, nicht für genaue Messungen dieser Art verwendet werden können. Die RCA 6655 Röhre ergab gute Resultate. Anwendungen auf Mischungen von Cr-151–J-131 und Na-24–K-42 wurden beschrieben.

WHEN using radioactive tracers of low activity in biological and medical problems, a need has very often arisen for using more than one radioactive substance at the same time. The problem of analysis then becomes complicated, but there are several ways in which isotopes in mixtures can be determined.

The method to be described is to discriminate between the different gamma energies of the isotopes, with a scintillation counter used as a spectrometer. This has been used mostly for identifying isotopes in e.g. activation analysis. The procedure is to scan the entire energy spectrum and if the resolution is adequate to use the calculated areas under the energy peaks as measures of the corresponding activities. This procedure is rather simple when the activities are high and the resolution good. CONNALLY and LEBOEUF[1] as early as 1953 performed analysis of radionuclide mixtures in this way. For a good description of the technique see CONNALLY.[2] When one of two nuclides has a photopeak well separated from the spectrum of the other a simple discrimination can be used.[3,4] Any spectrogram may be improved by using two crystals, one of NaI(Tl) and one of anthracene. The latter absorbs only the Compton photones, which can be subtracted from the Compton continuum plus the photopeaks detected in the NaI(Tl) crystal.[5] If, however, the isotopes have γ-energies which are very close together the procedure may become more difficult. A greater difficulty occurs however, when the activities are also far too low to be used for complete spectroanalysis. This very often happens in biological and medical samples, where the activities in general must be rather low because of health hazards.

The only way of determining activities in such samples is to use counters and count for a sufficient length of time. This gives rise, however, to problems which are a little different from those generally encountered in gammaspectrometry. A method will be described below which seems to be very useful in analysing mixtures of two radioisotopes, each of them in rather low activities.

THEORY

An analysis of a γ-energy spectrum of a decaying nuclide at different time intervals shows that the height of the curve, i.e. the counts/min at different energy levels, decreases uniformly throughout. That means that after one half-life period ($T_{\frac{1}{2}}$) every point of the curve has decreased to one half of its original level.

When analysing two radio nuclides A and B, it is necessary to count the activity at two different energy levels I and II. For the nuclide A the activity in channel I is $C_A{}^{\mathrm{I}}$ and in II is $C_A{}^{\mathrm{II}}$. If the half-life is short and the activities in the two channels cannot be determined simultaneously (e.g. with a single channel analyser) the activity in the channel determined last must be corrected. If the activities at the time when channel I is analysed ($t^{\mathrm{I}} = 0$) are denoted as C (counts/min), all actual countings in channel I and II as N^{I} and N^{II} and the time when they are determined as t^{I} (=0) and t^{II}; then

$$N^{\mathrm{I}} = C^{\mathrm{I}} \tag{1}$$

and

$$N^{\mathrm{II}} = k^{\mathrm{II}} C^{\mathrm{II}} \tag{2}$$

where

$$k^{\mathrm{II}} = \exp\left(-0{\cdot}69 t^{\mathrm{II}}/T_{\frac{1}{2}}\right) \tag{3}$$

According to the above equation

$$C_A{}^{\mathrm{I}}/C_A{}^{\mathrm{II}} = N_A{}^{\mathrm{I}}\left(k_A{}^{\mathrm{II}}/N_A{}^{\mathrm{II}}\right) = \\ = \text{constant} = q_A \tag{4}$$

$$C_B{}^{\mathrm{I}}/C_B{}^{\mathrm{II}} = N_B{}^{\mathrm{I}}\left(k_B{}^{\mathrm{II}}/N_B{}^{\mathrm{II}}\right) = \\ = \text{constant} = q_B \tag{5}$$

The constants q_A and q_B can consequently be determined from standard samples containing either A or B alone.

In analysing a *mixture* of A and B the following relations are apparent

$$N_{\text{tot}}^{\text{I}} = C_A{}^{\text{I}} + C_B{}^{\text{I}} \tag{6}$$

$$N_{\text{tot}}^{\text{II}} = k_A{}^{\text{II}} C_A{}^{\text{II}} + k_B{}^{\text{II}} C_B{}^{\text{II}} \tag{7}$$

where $N_{\text{tot}}^{\text{I}}$ and $N_{\text{tot}}^{\text{II}}$ are the total counts/min of the mixture in channel I (at $t^{\text{I}} = 0$) and channel II (at t^{II}) respectively. By combination of (4), (5), (6) and (7) we obtain

$$C_A{}^{\text{I}} = \frac{N_{\text{tot}}^{\text{I}} - (q_B/k_B{}^{\text{II}}) \cdot N_{\text{tot}}^{\text{II}}}{1 - (q_B/k_B{}^{\text{II}})(k_A{}^{\text{II}}/q_A)} \tag{8}$$

$$C_A{}^{\text{II}} = (1/k_A{}^{\text{II}}) \cdot \frac{N_{\text{tot}}^{\text{II}} - (k_B{}^{\text{II}}/q_B) N_{\text{tot}}^{\text{I}}}{1 - (q_A/k_A{}^{\text{II}})(k_B{}^{\text{II}}/q_B)} \tag{9}$$

$$C_B{}^{\text{I}} = \frac{N_{\text{tot}}^{\text{I}} - (q_A/k_A{}^{\text{II}}) N_{\text{tot}}^{\text{II}}}{1 - (q_A/k_A{}^{\text{II}})(k_B{}^{\text{II}}/q_B)} \tag{10}$$

$$C_B{}^{\text{II}} = (1/k_B{}^{\text{II}}) \cdot \frac{N_{\text{tot}}^{\text{II}} - (k_A{}^{\text{II}}/q_A) N_{\text{tot}}^{\text{I}}}{1 - (q_B/k_B{}^{\text{II}})(k_A{}^{\text{II}}/q_A)} \tag{11}$$

Note that q is a constant while k^{II} has a different value for each sample and can be calculated from (3).

Having selected the energy channels (vide infra) it is usually necessary to make one more correction. Suppose that the limits of the channel are located on a steep slope of the spectrogram. Then a slight long time drift in the pulse height amplification will cause a significant change of C in this channel. A comparison of identical samples analysed at two different occasions may then not be possible. This disadvantage can easily be overcome by calculating the total counts in the whole spectrum instead of in a channel. If the standard samples A and B that were used for determinations of q_A and q_B are counted also with the window "wide open", i.e. the integrated counts/min for the whole spectrum (here called channel III) the following relations can be deduced:

$$N^{\text{III}} = k^{\text{III}} C^{\text{III}} \tag{12}$$

$$k^{\text{III}} = \exp\,(-0{\cdot}69 t^{\text{III}}/T^{\frac{1}{2}}) \tag{13}$$

and if A and B in the mixtures were calculated as $C_A{}^{\text{I}}$ and $C_B{}^{\text{II}}$ respectively

$$(N_A^{\text{III}}/k_A^{\text{III}})/N_A{}^{\text{I}} = r_A \tag{14}$$

and

$$(N_B^{\text{III}}/k_B^{\text{III}})(k^{\text{II}}{}_B/N^{\text{II}}{}_B) = r_B \tag{15}$$

Multiplying the calculated $C_A{}^{\text{I}}$ with r_A and $C_B{}^{\text{II}}$ with r_B will then give the total counts of A and B respectively in the mixture at the time when this mixture was counted in channel I. It is also possible to read the sample in channel I and III or in II and III and calculate the C^{III} activities. In this case the correction with r will be omitted. One prerequisite is that the total counts/min (N^{III}) of the sample is not too high for the counting equipment. Finally the usual correction for the decay should be made for the comparison of different samples. When dealing with half-lives of about 8 days or longer the correction for decay is usually not necessary. k^{II} and k^{III} are unity when counting is performed in two or three channels simultaneously. If the half-lives are not too short and the counting times not too long t^{I}, t^{II} and t^{III} should be determined from the mid-point of the counting time in the corresponding channels.

In the simple cases where k^{II} and k^{III} are unity the equations (8), (9), (10) and (11) change to

$$C_A{}^{\text{I}} = \frac{N_{\text{tot}}^{\text{I}} - q_B \cdot N_{\text{tot}}^{\text{II}}}{1 - q_B/q_A} \tag{16}$$

$$C_A{}^{\text{II}} = \frac{N_{\text{tot}}^{\text{II}} - 1/q_B \cdot N_{\text{tot}}^{\text{I}}}{1 - q_A/q_B} \tag{17}$$

$$C_B{}^{\text{I}} = \frac{N_{\text{tot}}^{\text{I}} - q_A N_{\text{tot}}^{\text{II}}}{1 - q_A/q_B} \tag{18}$$

and

$$C_B{}^{\text{II}} = \frac{N_{\text{tot}}^{\text{II}} - 1/q_A \cdot N_{\text{tot}}^{\text{I}}}{1 - q_B/q_A} \tag{19}$$

respectively.

With mixtures of Cr^{51}/I^{131} ADAMS and WOODWARD,[6] CRANE *et al.*[7] and ADAMS *et al.*[8] used similar equations as also did GROOM *et al.*[9] for mixtures of P^{32}/I^{131}. The last group solved their equations by an electric analogue and fed the results, i.e. the partial activities, into recording instruments.

Very often it will be possible to extend the analysis to more than two radio nuclides

even if the separation is far from complete. In the case of three components D, E and F the following equations appear (no corrections for decay):

$$C_D^{\mathrm{I}} : C_D^{\mathrm{II}} : C_D^{\mathrm{III}} = q_D^{\mathrm{I}} : q_D^{\mathrm{II}} : 1 \quad (20)$$

$$C_E^{\mathrm{I}} : C_E^{\mathrm{II}} : C_E^{\mathrm{III}} = q_E^{\mathrm{I}} : q_E^{\mathrm{II}} : 1 \quad (21)$$

$$C_F^{\mathrm{I}} : C_F^{\mathrm{II}} : C_F^{\mathrm{III}} = q_F^{\mathrm{I}} : q_F^{\mathrm{II}} : 1 \quad (22)$$

$$N_{\mathrm{tot}}^{\mathrm{I}} = C_D^{\mathrm{I}} + C_E^{\mathrm{I}} + C_F^{\mathrm{I}} \quad (23)$$

$$N_{\mathrm{tot}}^{\mathrm{II}} = C_D^{\mathrm{II}} + C_E^{\mathrm{II}} + C_F^{\mathrm{II}} \quad (24)$$

$$N_{\mathrm{tot}}^{\mathrm{III}} = C_D^{\mathrm{III}} + C_E^{\mathrm{III}} + C_F^{\mathrm{III}} \quad (25)$$

From these equations the solution for any of the terms C may be found.

INSTRUMENTATION

From the theory just described it follows that samples containing a mixture of two radioisotopes should be counted in two fixed energy channels. To obtain reliable results this implies the necessity of an extremely stable amplification of the pulse heights so that the channels really can be called "fixed". A slight short time drift which is out of the control of the observer will upset the results. It was therefore necessary to test the counting equipment very carefully as regards both its short- and long-time stability. At our disposal we had a single channel pulse height analyser (Tracerlab's). In the first place it could be noticed that without a stabilizer for the power supply stability of the apparatus was inadequate. In our experiments we have been able to keep the supply at 228 V $\pm$ 0·2 per cent. Furthermore the high voltage for the photomultiplier tube had to be of high precision. We have used therefore in this work a Tracerlab precision high voltage supply which has a long-term stability of 0·02 per cent or better per day. Any other precision high voltage equipment is of course satisfactory, but it is imperative that all other equipment, especially the linear amplifier, must be of the highest quality and precision.

The first task in selecting the energy channels is to determine the energy spectrum of the isotopes. For this purpose we have built an apparatus which automatically scans over the desired range of the spectrum. The peaks of this spectrum, however, appear with a slight delay because of time lag resulting from the relationship between the speed of the scanning and the time constant of the ratemeter. In order to correct for this lag the scanning device has been so constructed that it automatically scans back and forth until it is stopped. This means that in one direction the lag will cause the peak to appear to lie in a too high energy region whereas in the other direction it will appear equally displaced towards the lower energy region. Thus the average position of the peak can easily be determined. Fig. 1 shows the result of such a scanning back and forth over the peak of Cs^{137} (0·662 MeV). The vertical marks on the spectrographic curve denote every 10 V on the discriminator setting of the pulse height analyser.

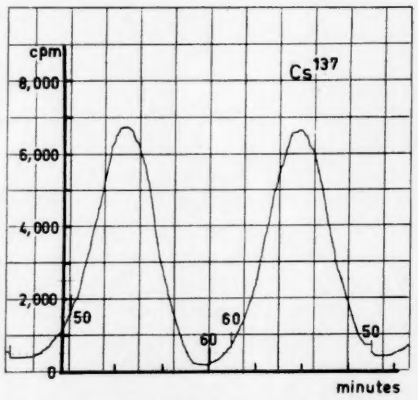

FIG. 1. A curve obtained from a to and fro scanning over the photopeak of Cs^{137}. The vertical lines marked 50 and 60 denote 50 and 60 V on the discriminator settings. The direction of scanning was changed between 60–60. Time constant of the ratemeter = 10 sec.

Because of the low activities usually employed a well-type $1\frac{3}{4}$ in. NaI(Tl) crystal was used. This gives a good geometry. On the other hand the resolution with such crystals is usually much lower than with flat crystals. The resclution, however, also depends on the photomultiplier tube as will be seen below.

TEST OF STABILITY

After finding the position of the energy peaks a test of stability was undertaken in such a way that samples were counted with a narrow window width at the steepest part of the slope. Slight changes in pulse height amplification are then manifest by either decreased or increased counting rates. In our first experiments we used a Dumont 6292 photomultiplier tube. This tube has silver magnesium dynodes and according to BELL[10,11] all such tubes show a change of pulse height with changes in counting rates. This serious defect was found also in our tube as can be seen in Fig. 2. In this case a sample of Cs^{137} was repeatedly counted after having been in the crystal well for at least 1 hr. Only statistically insignificant variations in the results were recorded at every counting. If, however, the sample was taken out 3 min in between each counting the sloping curve in Fig. 2 was obtained showing that some kind of a "fatigue" effect occurred. The pulse height actually decreased for decreasing counting rates. Usually it took more than 60 min before the tube reached stability. We therefore tested another tube, RCA 6655, which did not show these defects, but attained a stable counting rate within a few seconds.

It was pointed out above that the resolution is not too good with a well-type crystal and therefore the results could be considered to be very satisfactory when the resolution obtained in the case of Cs^{137} was about 13 per cent with a Dumont 6292 and about 10 per cent with a RCA 6655.

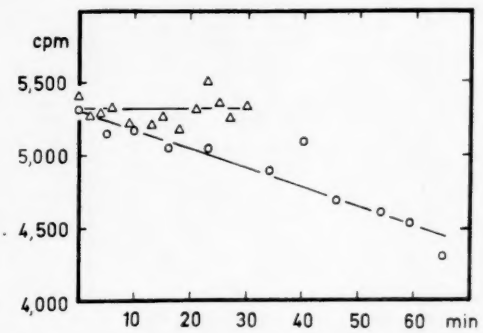

FIG. 2. A sample of Cs^{137} counted repeatedly after having been in the crystal well for more than 60 min (△). When the same sample was taken out of the well for 3 min in between every counting the sloping line appeared (○). Photomultiplier tube Dumont 6292.

APPLICATIONS

Experiments will be described in which Cr^{51} and I^{131} on the one hand and Na^{24} and K^{42} on the other were analysed in mixtures.* Fig. 3 shows the two spectral curves over the main peaks of Cr^{51} and I^{131}. In our experiments we chose the two channels marked as dotted areas in this figure. This means that in channel I most of the chromium was counted and only a small part of the iodine whereas in channel II the opposite was the case. By using these two channels and calculating according to the formulae given above (with k^{II} and k^{III} taken as unity) the results in Fig. 4 and Fig. 5 were obtained. In Fig. 4 a mixture of Cr^{51} and I^{131} was diluted so that the proportion between the two radionuclides was the same in every sample. In Fig. 5 the chromium was kept constant at a counting rate of

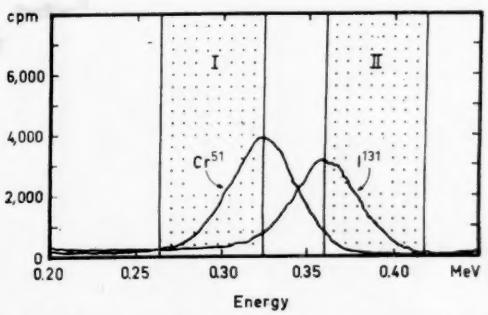

FIG. 3. The spectral curves for Cr^{51} and I^{131}. The dotted areas show the two channels in which a mixture of the two nuclides were counted.

* Cr^{51} and I^{131} were obtained from the Radiochemical Centre, Amersham, England. Na^{24} and K^{42} were kindly supplied by A. B. Atomenergi, Stockholm.

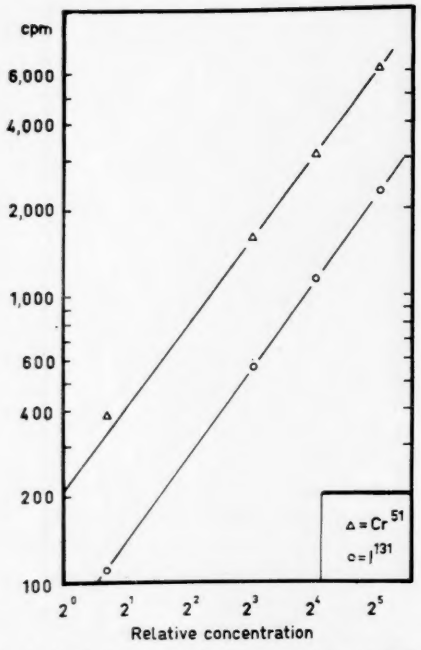

FIG. 4. Analysis of a mixture of Cr^{51} and I^{131}. Two observations above each other refer to the same sample.

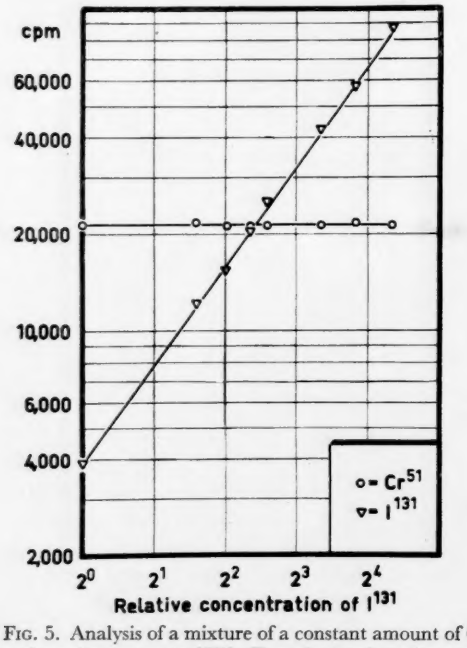

FIG. 5. Analysis of a mixture of a constant amount of Cr^{51} and varying amount of I^{131}. Two observations above each other refer to the same sample.

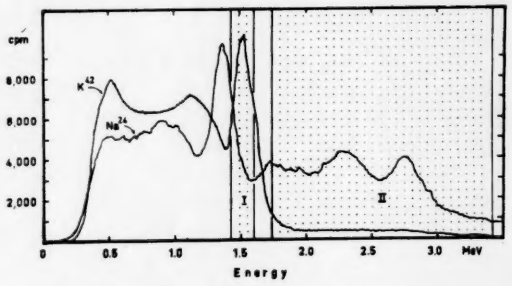

FIG. 6. The spectral curves for Na^{24} and K^{42}. The dotted areas show the two channels in which a mixture of the two nuclides was counted.

about 20,000 counts/min whereas iodide changed from about 90,000 counts/min down to 4000 counts/min.

In the next series of experiments Na^{24} and K^{42} were used and the two spectrograms are shown in Fig. 6. The two channels are shown by the dotted areas. In channel I most of the potassium and some sodium was counted, whereas in channel II very nearly sodium alone was recorded. In Fig. 7 similar results as were obtained for chromium and iodine in Fig. 4 are shown. It can be seen also here that dilution gives consistent ratios of the two isotopes. Figs. 8 and 9 show the results of experiments in which either the potassium or sodium was kept at the constant

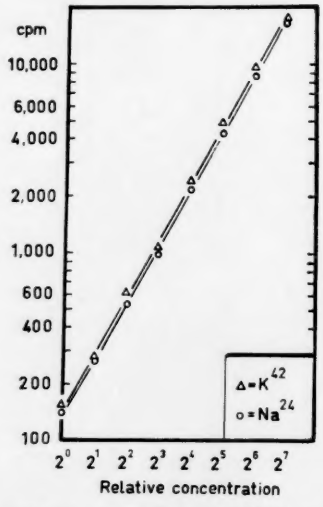

FIG. 7. Analysis of a mixture of Na^{24} and K^{42}. Two observations above each other refer to the same sample.

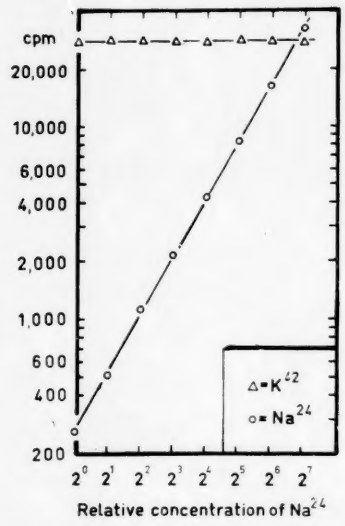

FIG. 8. Analysis of a mixture of a constant amount of K^{42} and varying amount of Na^{24}. Two observations above each other refer to the same sample.

high level whereas the other radioactive nuclide was diluted to counting rates as low as 150 counts/min. In the case of a constantly high potassium and varying sodium level it is quite obvious that the curve for sodium passes through the origin, (a straight line in the semilogarithmic graph), whereas in Fig. 9 the curve for K^{42} does not pass through the origin and could therefore not be drawn as a straight line on semilogarithmic paper. This discrepancy has not yet been explained.

The above results indicate a useful method of determining radioactive isotopes in mixtures by gammaspectrometry in fixed energy channels even if the peaks of the spectrograms as in the above example are not well separated and if the activities are much too low to be useful for complete spectrographic analysis. Theoretically the analysis of more than two isotopes in mixtures presents little difficulty. It is not uncommon to analyse five components in mixtures if the energy distributions are suitable. An absolutely necessary requirement is an equipment which is extremely stable as regards pulse height amplification (this implies the avoidance of silver magnesium dynodes in the photomultiplier).

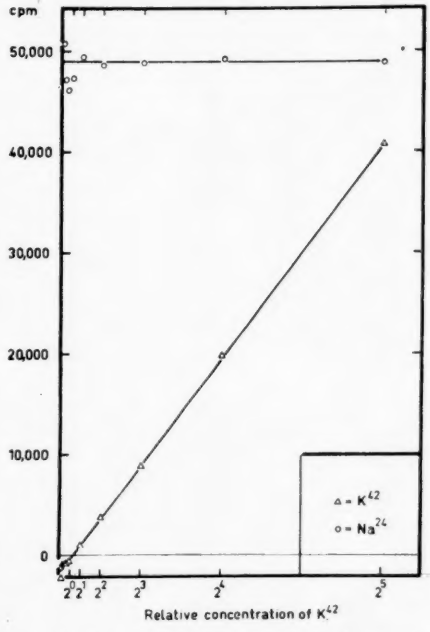

FIG. 9. Analysis of a mixture of a constant amount of Na^{24} and varying amount of K^{42}. Two observations above each other refer to the same sample. For an unknown reason the curve for K^{42} does not pass through the origin.

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Investigation of Isotope Exchange Reactions between Organic Iodides and Iodide Ions

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The kinetics of the isotopic exchange taking place at 56°C between ethyl, *n*-propyl, *n*-butyl, 2-phenylethyl, 3-phenylpropyl and 4-phenylbutyl iodides and potassium iodide labelled by I^{131} in absolute ethanol were examined. With the use of the kinetic curves, the rate constants were calculated. An appreciable decrease in rate constant and hence in reactivity was observed with increasing number of carbon atoms in the chain.

The changes in activation energies occurring with increasing number of carbon atoms of the chain were established.

INVESTIGATION SUR LES RÉACTIONS D'ECHANGE ISOTOPIQUE ENTRE LES IODURES ORGANIQUES ET LES IONS D'IODURE

La kinétique de l'échange isotopique qui a lieu à 56°C entre les iodures éthylique, *n*-propylique, *n*-butylique, 2-phényléthylique, 3-phénylpropylique et 4-phénylbutylique et l'iodure de potassium marqué de l'I^{131} fut examiné. Les constantes de taux furent calculées au moyen des courbes kinétiques. Une diminution considérable de la constante de taux, ainsi de la réactivité, avec augmentation du nombre des atomes de carbone dans la chaîne fut remarquée.

Le changement des énergies d'activation prenant lieu avec augmentation du nombre d'atomes de carbone la chaîne fut établi.

ИССЛЕДОВАНИЕ РЕАКЦИЙ ИЗОТОПНОГО ОБМЕНА МЕЖДУ ОРГАНИЧЕСКИМИ ИОДИДАМИ И ИОНАМИ ИОДИДОВ

Была исследована кинетика изотопного обмена между иодидами этила, н-пропила, н-бутила, 2-фенилэтила, 3-фенилпропила и 4-фенилбутила и иодистым калием, меченым I^{131}, при 56°C в абсолютном спирте. Константы скорости были вычислены по кинетическим кривым. При увеличении числа атомов углерода в цепи наблюдалось заметное уменьшение констант скорости и, соответственно, реакционной способности.

Были определены изменения энергии активации с увеличением числа атомов углерода в цепи.

UNTERSUCHUNGEN VON ISOTOPENAUSTAUSCH-REAKTIONEN ZWISCHEN ORGANISCHEN IODIDEN UND IODIDIONEN

Die Kinetik des Isotopenaustausches bei 56°C zwischen Äthyl-, *n*-Propyl-, *n*-Butyl-, 2-Phenyläthyl-, 3-Phenylpropyl-, 4-Phenylbutyl-jodid und J-131-markiertem Kaliumjodid in absoluten Äthylalkohol wurde untersucht. Durch Verwendung von Kinetikkurven wurden die Geschwindigkeitskonstanten ausgerechnet. Mit steigender Anzahl der Kohlenstoffatome in der Kette wurde eine merkliche Abnahme der Reaktionskonstanten und daher auch der Reaktivität beobachtet.

Veränderungen der Aktivierungsenergien mit zunehmender Anzahl der Kohlenstoffatome der Kette wurden bestätigt.

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Reactions of isotopic exchange between organic iodine compounds and potassium iodide have long been studied. The rate constants of these processes,[1,2,5] the effect of solvent on the progress of the reactions[3] and the influence of various cations such as K, Na, Li, etc.,[4] were determined and, on the basis of experimental data, the equations describing these processes were evolved.[6,7]

Although these investigations were extended to numerous organic halides including aliphatic, aromatic, substituted aromatic and alicyclic iodides,[8] arylalkyl iodides, with the exception of benzyl halides,[9] are not mentioned in the literature as having been used as model substances. However, benzyl halides show in exchange reactions and in other chemical processes (hydrolysis) properties differing from those of the higher homologues of the arylalkyl series.

Recently, the reactions of this type were repeatedly examined to establish the effect of the variation of the organic radical on their kinetics.[10,11]

The scope of the present experiments was similar, in that isotopic exchanges of six organic iodine compounds were measured under completely identical conditions of temperature, solvent and concentration.

The results obtained served as a basis in drawing conclusions with regard to the reactivity of the organic radical and in characterizing this property by quantitative data.

EXPERIMENTAL METHODS

Exchange reactions were studied in the apparatus shown in Fig. 1. The solution of alkyl iodide in dry ethanol was introduced into reaction vessel *A*. When the system had reached the desired temperature, a solution of KI, also adjusted to the desired temperature, was added from flask *B*. Samples were taken with the use of pipet *C*, through which an air current was passed into the liquid when stirring was needed. An ultrathermostat served for keeping the temperature constant in view of the known sensitivity of exchange reactions to fluctuations of temperature. It appeared satisfactory to take, in the course of a reaction, 6–8 samples for establishing the kinetic curves.

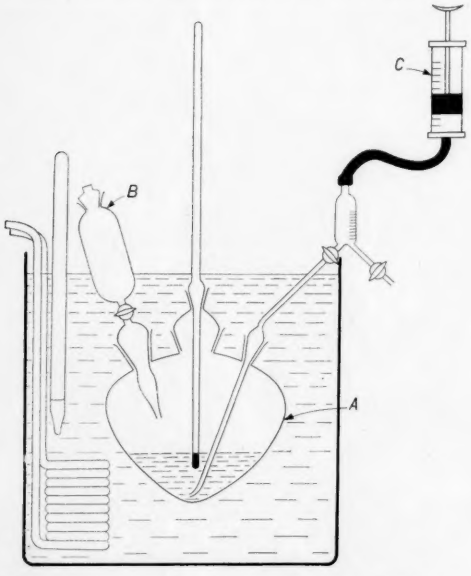

Fig. 1. Apparatus for the investigation of exchange processes (see text).

The samples were quickly shaken with benzene and water. Shaking was repeated three times. Preliminary tests proved that no more shakings are necessary as no residual activity could be detected in the aqueous phase.

Other authors[4] have shown that identical results are obtained by measuring the specific activity of either potassium iodide or organic iodide. It seemed more practical to measure increasing activities, i.e. the activity of the organic iodide. Therefore, the benzene phases obtained on shaking were further processed.

Iodide was precipitated by ethanolic silver nitrate. On allowing to stand for a day, quantitative precipitation was attained without heating.

The precipitated AgI was filtered through a glass filter of about 2·5 cm^2 surface, washed with methanol and water and dried as prescribed. The activity of dried precipitate was measured in the glass filter itself.

Thus, care was taken to obtain a steady layer thickness during filtering.

Activity was measured with a mica window Geiger-Müller counter (window thickness ~8 mg/cm²) under constant geometrical conditions. The self-absorption and self-scattering of the precipitate were taken into account by the use of a calibration curve. It was not necessary to determine absolute activities. However, the specific activity of the original KI was regularly measured and these values used when caclulating the data of x/c (see later on).

Substances

Ethyl, *n*-propyl, *n*-butyl, 2-phenylethyl, 3-phenylpropyl and 4-phenylbutyl iodides were prepared by direct iodination of the corresponding alcohols in the presence of red phosphorus.[12] Crude iodides were purified in the conventional way and distilled at reduced pressure.

3-Phenylpropyl alcohol was obtained by reducing hydrocinnamic ethylate with $LiAlH_4$. b.p.$_{12}$: 119°C.

4-Phenylbutyl iodide was prepared as follows. Benzoyl propionic acid obtained from benzene and succinic anhydride by the Friedel-Crafts reaction was purified by recrystallization and re-precipitation, m.p. 115°C. Benzoyl propionic acid was reduced according to Clemmensen to 3-phenyl butyric acid, m.p. 48°C. 3-Phenyl butyric acid was converted to ethylate and reduced by $LiAlH_4$. The 4-phenylbutyl alcohol obtained was subjected to repeated distillations under reduced pressure. b.p.$_{12}$: 125–126°C.

The purity of alkyl iodides met the usual requirements. Their concentration was 0·2 mole/l. whereas the KI solution was saturated (corresponding to 0·105 mole/l. at room temperature in dry ethanol). Radioactive iodide was available in an aqueous solution, in the form of KI. A portion of the aqueous solution containing the required activity was evaporated to dryness and dissolved in the saturated ethanolic solution of KI. The activity of the ethanolic KI solution was about 20 μc/100 ml.

All experiments were carried out at 56°C.

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EXPERIMENTAL RESULTS

Kinetic curves of the isotopic exchange of ethyl, propyl and butyl iodides are shown in Fig. 2.

The exchange process may be formulated as

$$RX + X^{*-} \rightleftharpoons RX^* + X^- \qquad (1)$$

i.e. the reaction proceeds according to a molecular–ionic mechanism. In this case, the equation

$$W \equiv \frac{dx}{dt} = kfa(c - x) - kfbx \qquad (2)$$

should be applied[10,11] to describe the reaction rate, where $x = [RX^*]$ impulses/min g, $a = [RX]$ mole/l., $b = [X^-]$ mole/l., $c = [RX^* + X^{*-}]$ impulses/min g, $f =$ activity coefficient of I ion in dry ethanol.

The rate constant is obtained by integration of equation (2):

$$k = -\frac{2{\cdot}3}{(a+b)ft}\log\left[1 - \left(1 + \frac{b}{a}\right)\frac{x}{c}\right] \qquad (3)$$

As values of x/c were obtained in our experiments, it seemed practical to convert equation (3) into the form:

$$\frac{1}{c}\cdot\frac{dx}{dt} = kf\left(a - a\frac{x}{c} - b\frac{x}{c}\right) \qquad (4)$$

Values $\frac{1}{c}w$ calculated $\left(w = \frac{dx}{dt}\right)$ with this equation are presented in Fig. 3. Prior to plotting the rate curves shown in Fig. 3, it was necessary to determine the values of rate constant k and activity coefficient f. For this purpose, values of

$$-\log\left[1 - \left(1 + \frac{b}{a}\right)\frac{x}{c}\right] = Y \qquad (5)$$

were plotted against time (Fig. 4).

The slope of the lines yields the product kf

$$kf = \frac{\Delta Y}{\Delta t}\cdot\frac{2{\cdot}3}{(a+b)}\cdot\frac{1}{60} \qquad (6)$$

(The term 1/60 is necessary in order to obtain c.g.s. units.)

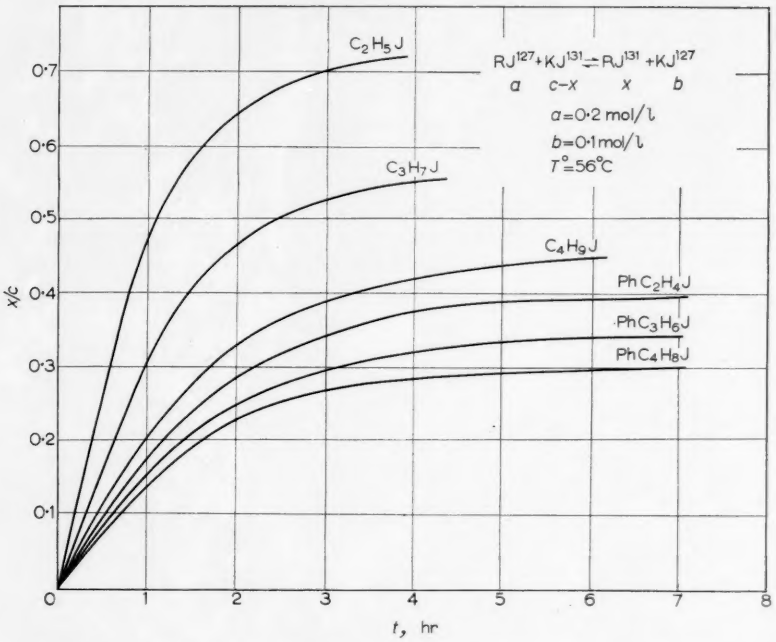

FIG. 2. Data of isotopic exchange of alkyl and aralkyl iodides plotted against time.

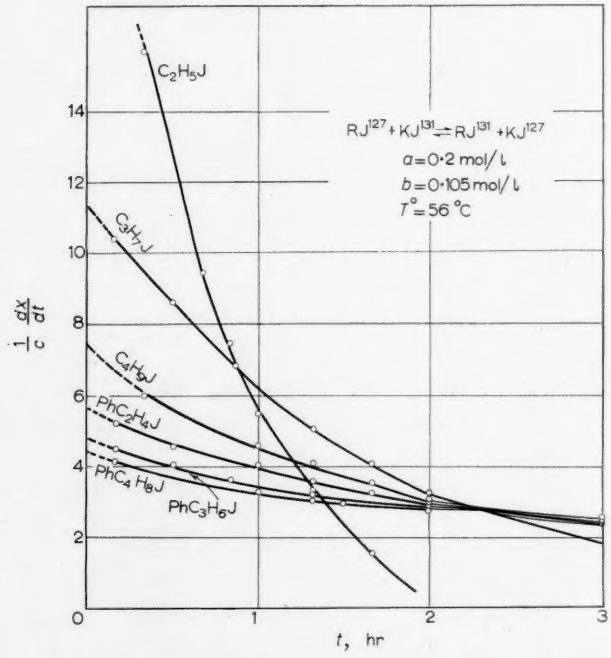

FIG. 3. Curves of exchange rates of alkyl and aralkyl iodides according to equation (4).

Values of f were determined by measuring the electrical conductance of KI solutions in dry ethanol (cf. Table 1) and calculating f

TABLE 1

c mole/l.	$\kappa \cdot 10^4 \Omega^{-1}$	$\lambda = \frac{1000}{c}\kappa$	$f = \frac{\lambda}{\lambda_\infty}$
0·105 (saturated)	2·52	2·39	0·23
0·0025	0·26	10·40	

values from the results. With the use of values of f and products kf, the rate constants and the corresponding rates can be obtained.

TABLE 2a. Data of the exchange reaction $CH_3CH_2I^{127} + KI^{131}$

t (min)	x/c	Y cf.eq.(5)	$\frac{1}{c}w \cdot 10^5$
5	0·100	0·0719	18·10
15	0·200	0·158	14·87
25	0·290	0·254	12·31
35	0·365	0·347	9·60
45	0·418	0·455	7·81
55	0·480	0·573	5·78
70	0·555	0·903	3·32
90	0·605	1·114	1·66
110	0·640	1·602	
135	0·678		
165	0·700		

TABLE 2b. The same, with propyl iodide

t (min)	x/c	Y cf.eq.(5)	$\frac{1}{c}w \cdot 10^5$
5	0·068	0·047	10·61
20	0·17	0·131	8·76
40	0·27	0·231	6·99
55	0·31	0·279	6·24
70	0·38	0·374	4·98
90	0·43	0·463	4·08
110	0·47	0·548	3·37
135	0·51	0·638	2·72
165	0·53	0·687	1·35
195	0·55	0·774	1·18
225	0·55	0·795	1·13
255			
285			

The measured and calculated values for all six organic iodides are presented in Table 2.

Table 3 shows the k values established by us for alkyl and arylalkyl iodides.

It appears from the data in Table 3 that the relative decreases in the values of k are much smaller for the arylalkyl series than for the alkyl iodides. Differences in the rate constants for butyl iodide and phenylethyl iodide appear to approximate very closely the differences in k values for butyl iodide and amyl iodide, i.e. an aliphatic chain of this type affects the reaction in the same way as the phenyl radical does. On the other hand, in the arylalkyl series, the effect of the phenyl radical on the reaction decreases with increasing length of the side chain.

Similar conclusions can be drawn from the comparison of initial rates (Table 4).

TABLE 2c. The same, with butyl iodide

t (min)	x/c	Y cf.eq.(5)	$\frac{1}{c}w \cdot 10^5$
10	0·070	0·049	6·02
25	0·100	0·072	5·70
45	0·195	0·154	4·72
70	0·250	0·209	4·17
90	0·294	0·258	3·71
110	0·325	0·298	3·39
135	0·370	0·362	2·93
165	0·390	0·394	2·44
195	0·408	0·424	1·52
225	0·422	0·449	1·44
285	0·430		
315	0·438		

TABLE 2d. The same with 2-phenylethyl iodide

t (min)	x/c	y*	$\frac{1}{c}w \cdot 10^5$
5	0·035	0·9466	5·23
20	0·095	0·855	4·72
45	0·180	0·726	4·00
70	0·210	0·680	3·75
90	0·258	0·607	3·34
110	0·288	0·561	3·09
135	0·328	0·500	2·76
165	0·352	0·464	2·56

* $Y = -\log y$

TABLE 2e. The same with 3-phenylpropyl iodide

t (min)	x/c	y^*	$\frac{1}{c} w \cdot 10^5$
5	0·035	0·9466	4·62
20	0·090	0·863	4·22
45	0·160	0·756	3·69
75	0·215	0·672	3·28
105	0·253	0·614	2·99
135	0·280	0·573	2·81
165	0·300	0·542	2·65
190	0·310	0·527	2·54

TABLE 2f. The same with 4-phenylbutyl iodide

t (min)	x/c	y^*	$\frac{1}{c} w \cdot 10^5$
5	0·025	0·959	4·14
20	0·079	0·879	3·80
45	0·140	0·786	3·38
75	0·190	0·710	3·09
105	0·230	0 649	2·80
135	0·252	0·616	2·68
165	0·270	0·588	2·55
190	0·275	0·580	2·41

In order to facilitate comparison, values of rate constants with respect to the rate constant of ethyl iodide are summarized in Table 5. These values show directly the "relative reactivities" of the corresponding radicals, referred to the ethyl radical. As the third column of Table 5 indicates, the relative initial rates give the same results.

TABLE 3

RI	$k \cdot 10^4$ l. mole^{-1} sec^{-1}
CH_3–CH_2–I	46·7
CH_3–CH_2–CH_2–I	25·7
CH_3–CH_2–CH_2–CH_2–I	14·6
C_6H_5–CH_2–CH_2–I	12·0
C_6H_5–CH_2–CH_2–CH_2–I	10·6
C_6H_5–CH_2–CH_2–CH_2–CH_2–I	9·4

TABLE 4

RI	w_0 sec^{-1}	x/c
CH_3–CH_2–I	21	0·72
CH_3–CH_2–CH_2–I	11·4	0·55
CH_3–CH_2–CH_2–CH_2–I	7·4	0·45
C_6H_5–CH_2–CH_2–I	5·6	0·39
C_6H_5–CH_2–CH_2–CH_2–I	4·8	0·34
C_6H_5–CH_2–CH_2–CH_2–CH_2–I	4·4	0·30

The present experiments were carried out at a single temperature. Thus, it was not possible to determine activation energies by

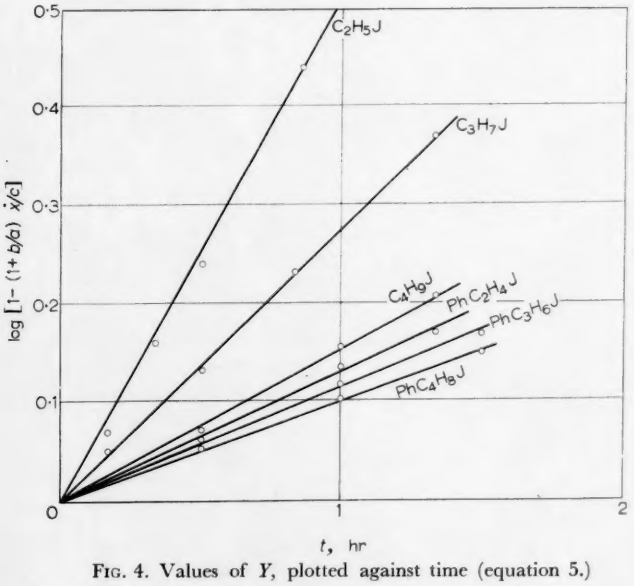

FIG. 4. Values of Y, plotted against time (equation 5.)

TABLE 5

RI	$\frac{k}{k_{eth}}$	$\frac{w_0}{w_{0_{eth}}}$
CH_3–CH_2–I	1·00	1·00
CH_3–CH_2–CH_2–I	0·55	0·54
CH_3–CH_2–CH_2–CH_2–I	0·31	0·35
C_6H_5–CH_2–CH_2–I	0·257	0·258
C_6H_5–CH_2–CH_2–CH_2–I	0·227	0·229
C_6H_5–CH_2–CH_2–CH_2–CH_2–I	0·206	0·208

TABLE 6

R	ΔE, cal.
CH_3–CH_2–	0
CH_3–CH_2–CH_2–	391
CH_3–CH_2–CH_2–CH_2–	757
C_6H_5–CH_2–CH_2–	882
C_6H_5–CH_2–CH_2–CH_2–	965
C_6H_5–CH_2–CH_2–CH_2–CH_2–	1040

direct measurements. However, with the use of known values of k, differences in activation energies can be calculated. Namely, the correlation

$$\log \frac{k_1}{k_2} = \frac{\Delta Q}{2{\cdot}3RT} \qquad (7)$$

is approximately valid. In this way, changes in the activation energy with increase of carbon chain length (or, more exactly, changes in the activation energy and entropy of the intermediate complex) can be obtained. Data are presented in Table 6.

It can be seen from the data that for the arylalkyl series the changes in ΔE values with increase in the number of carbon atoms in the side chain are much smaller, than for the alkyl iodide series.

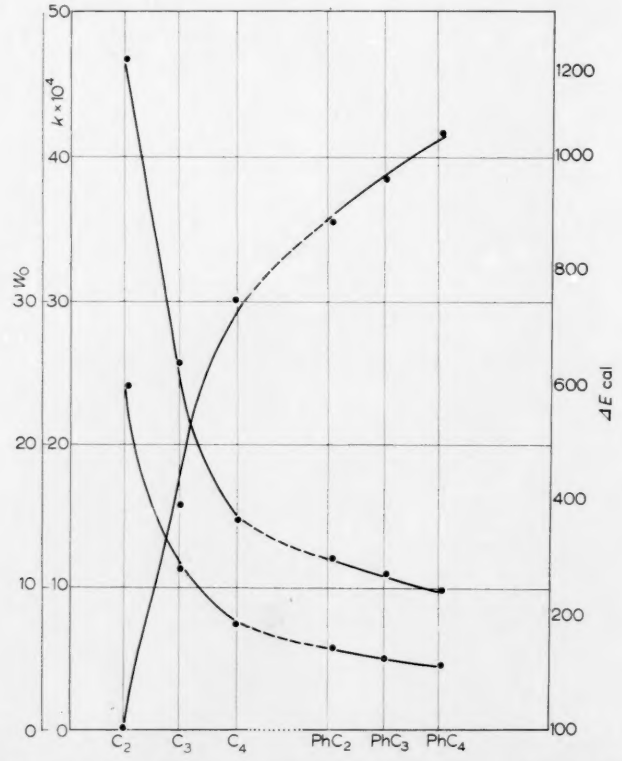

FIG. 5. Differences in the values of rate constants, of initial rates and of activation energies plotted against the number of carbon atoms.

Fig. 5 shows the values w_0, k and ΔE plotted against the number of carbon atoms. It appears from the curves that, in the reactions studied, the phenyl radical exerts an effect similar to that expected for the higher homologues (over C_5) of the alkyl series.

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Recoil Tritium Labelling of Deuterated Compounds

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An attempt is made to evaluate H/D isotope effects in the recoil tritiation process by comparing the distribution of tritium found in *iso*propyl benzoate with that found in deuterated species. The observed H/D isotope effects are small, 1·41 for tritiation at a methyl group, and 1·16 for tritiation in the ring. As in other cases tritiation at ring positions occurs with higher efficiency, in terms of survival of intact molecules, than for tritiation in the alkyl group.

LE MARQUAGE DES COMPOSÉS DEUTÉRÉS AVEC LE TRITIUM DE RECUL

On essaie d'évaluer les effets isotopiques H/D dans le procédé de la tritiation à recul, en comparant la distribution du tritium trouvée dans le benzoate isopropylique avec celle trouvée dans les espèces deutérées. Les effets isotopiques H/D qu'on observe sont minuscules, 1,41 pour la tritiation à un group méthylique, et 1,16 pour la tritiation au cercle. Comme en d'autres cas la tritiation aux locations dans le cercle prend lieu avec une efficacité, mesurée par la survivance des molécules intactes, supérieure à celle pour la tritiation dans le groupe alcoyl.

МЕТКА АТОМАМИ ОТДАЧИ ТРИТИЯ ДЕЙТЕРОСОДЕРЖАЩИХ СОЕДИНЕНИЙ

Сделана попытка определить изотопные эффекты H/D в процессах введения атомов отдачи трития по сравнительному распределению трития в изопропилбензоате и дейтеросодержащих соединениях. Наблюденные изотопные эффекты H/D малы; 1,41 при введении трития в метильную группу и 1,16 при введении трития в кольцо. Как и в других случаях, введение трития в кольцо более эффективно с точки эрения выживания интактных молекул, чем введение трития в алкильную группу.

MARKIERUNG VON DEUTERIUM ENTHALTENDEN VERBINDUNGEN DURCH TRITIUM-RÜCKSTOSS

Durch Vergleich der in Isopropyl-Benzoaten aufgefundenen Tritiumverteilung, mit der, welche in den deuteriumhältigen Species gefunden wurde, wurde versucht, die H/D Isotopeneffekte für die Tritium-Rückstossmarkierung heranzuziehen. Die beobachteten H/D-Isotopeneffekte sind klein: 1,41 für die Überführung von Tritium in eine Methylgruppe und 1,16 für Aufnahme von Tritium im Ring. Ebenso wie in anderen Fällen erfolgt die Aufnahme von Tritium in Ringpositionen mit grösserer Ausbeute in bezug auf das Überleben von ganzen Molekülen, als die Aufnahme von Tritium in die Äthylgruppe.

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INTRODUCTION

In the expectation that H/D isotope effects would provide criteria permitting some conclusions as to the mechanisms operating in the recoil tritiation of organic materials by the method of Wolfgang *et al.* and Rowland and Wolfgang[1,2] experiments have been performed on the distribution of tritium in irradiated *iso*propyl benzoate and in variously deuterated forms of *iso*propyl benzoate. Inability to reproduce or to determine exactly the neutron dosages in separate experiments required that the H/D isotope effects be evaluated not by measurements of the total tritium incorporation in normal versus fully deuterated compounds but by comparisons of normal versus selectively deuterated species wherein the undeuterated portion of the molecule serves as an internal standard. The selectively deuterated species were *iso*propyl benzoate-d_5 and *iso*propyl-d_6 benzoate thus permitting a comparison of averaged H/D isotope effects for the replacement of ring and alkyl hydrogens.

During the irradiations of the ester systems, small amounts of labelled polymeric by-products were also obtained. Partial tritium distribution studies performed with these polymers yielded valuable information concerning the mechanism of by-product formation.

EXPERIMENTAL*

Analytical procedures

Deuterium. The Graff and Rittenberg procedure[3] was used for deuterium analyses. In order to overcome memory effects in the combustion line, four 5 mg aliquots were combusted for each sample, the deuterium gas from the last two combustions being analyzed in the mass spectrometer. Before combustion each sample was diluted with non-isotopic material to give an α value of 0·65–0·70. (α = m.e.D/m.e.(D + H).) Accuracy to 1 per cent deuterium was achieved in the analytical procedure, the mass spectrometer being calibrated against standard deuterium samples.

Tritium. The one-step method[4] was used for the quantitative conversion of tritium in organic compounds to a mixture of hydrogen and methane.

Samples were heated for 3 hr at 650°C in evacuated glass tubes (1720 Pyrex glass), containing 40 mesh zinc†, nickelic oxide and water. Under these conditions 99 per cent of the original tritium was converted into gas whose activity was determined by transferring a known aliquot to an ionization chamber and measuring the ion-current by means of a vibrating reed electrometer.[5]

Reproducibility of approximately 1 per cent in tritium assay for samples of the same material was obtained. The absolute accuracy of the assay was probably good to 3 per cent.

Preparation of the compounds

Iso*propyl benzoate* was synthesized by esterifying benzoic acid with an excess of *iso*propanol in the presence of catalytic amounts of concentrated sulfuric acid. The ester was distilled twice before use. b.p. 217–8°C; n_d^{20} 1·4949.

Iso*propyl-d_6 benzoate* was prepared by the benzoylation of *iso*propanol-d_6 (propane-1,1,1,3,3,3-d_6-2-ol) which had been synthesized from the lithium aluminum hydride reduction of acetone-d_6.

Acetone-d_6 was obtained by equilibrating 30 g of spectrograde acetone with 15 g of deuterium oxide (99·5% D) in the presence of 0·1 g anhydrous potassium carbonate. Five such passes yielded acetone which was 91·6% deuterated, whilst twelve such exchanges gave a product which was 99·1% deuterated in the methyl groups. The samples of acetone were analyzed for deuterium as the 2,4-dinitrophenylhydrazones,

* All melting points were performed on a calibrated hot stage melting point apparatus.
† "Baker's Analyzed" Blue Label zinc metal—low in Pb and Fe.

prepared using KAPLAN's[6] procedure where maximum loss of isotope has been shown to be 0·2 per cent. In this method, acetone is added drop-wise to a stirred, ice-cold, saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid, the mixture kept at 0°C for 1 hr, then filtered, the precipitate being washed with ice-cold 2 N hydrochloric acid till colorless, then with cold water. The acetone-2,4-dinitrophenylhydrazone was recrystallized three times from methanol. m.p. 121–2°C.

Iso*propanol-*d_6 was synthesized by the reduction of acetone-d_6 with lithium aluminum hydride.

Iso*propyl-*d_6 *benzoate*. *Iso*propanol-d_6 (6·6 g) was added slowly with stirring and cooling to benzoyl chloride (12·6 ml) and pyridine (12 ml) in ether (50 ml). After working up the products in the usual manner, *iso*propyl-d_6 benzoate (6·8 g) containing deuterium corresponding to 98·9% deuteration of the methyl groups, was obtained. n_D^{20} 1·4950.

Iso*propyl benzoate-*d_5. A mixture of 13·8 ml *iso*propanol (Reagent Grade, Merck) and 6·25 g benzoic acid-d_5* was refluxed for 2 hr in the presence of 1·0 ml concentrated sulfuric acid. After separation and purification of the ester in the usual fashion, *iso*propyl benzoate-d_5 was obtained in 96 per cent yield (based on the benzoic acid-d_5 consumed). Analysis indicated that 99·2 per cent of the ring positions contained deuterium. n_D^{20} 1·4946.

Irradiation procedure

All irradiations were performed in the Isotope Trays of the CP-5 Reactor at Argonne National Laboratory at a flux of approximately $1{\cdot}0 \times 10^{12}$ neutrons/cm²/sec for periods of 118 to 153 hr. Liquid samples (*iso*propyl benzoate and deuterated derivates) were irradiated as the gels, formed by rapidly heating a mixture with lithium myristate to 200°C and quickly cooling. Control experiments showed that no *trans*-esterification or deuterium exchange occurred under the conditions employed.

Radiation decomposition of esters

Blank irradiations were performed by subjecting the various esters to pile irradiation for the same period of time as the tritiated species. With each compound, the degree of decomposition was exceedingly small (≈0·1 per cent), only very faint yellowing occurring at the completion of irradiation. These results are to be expected in view of the demonstration reported by ROWLAND and WOLFGANG,[2] that most of the radiation damage in recoil tritium processes of this type is done by recoiling alphas and tritons; little is attributed to the neutron and gamma flux of the pile.

Radiation-induced deuterium exchange in esters

Deuterium analyses on the deuterated *iso*propyl benzoate degradation products (i.e. *iso*propanol, acetone, benzoic acid) indicated that, within the limits of mass spectrometric measurement, neither inter- nor intra-molecular deuterium exchange had occurred during irradiation.

Opening of ampoules

The ampoules were opened in a calibrated vacuum line, the activity of the gas being measured by expanding a known aliquot into a calibrated ionization chamber in which the ion-current was measured by a Keithley electrometer. The total volume (corrected to s.t.p.) and pressure of gas present in the ampoules at the completion of the irradiation was calculated by means of conventional pressure–volume expansions in the calibrated line.

Recovery of iso*propyl benzoate from irradiated mixtures*

The gel which had become yellow during the irradiation process, was transferred to a centrifuge tube and extracted successively with ether and with acetone (two 5 ml portions of each). Lithium myristate was recovered by successive centrifugation and recrystallization of the residue from aqueous alcohol, although the weight of lithium

* For the synthesis of this compound see BROWN and GARNETT.[7]

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myristate was not sufficient to enable recrystallization of the material to be performed to constant specific activity.

The viscous liquid remaining after evaporation of the combined ether–acetone extract, upon vacuum distillation, yielded essentially pure *iso*propyl benzoate and a brown non-distillable oil (polymeric material). Molecular weight studies (cryoscopic, in benzene) yielded a value of 311 for the polymer obtained from non-deuterated *iso*propyl benzoate.

Treatment of polymers

A detailed infra-red analysis* was performed on each of the polymers prior to any degradation experiments. The following evidence was obtained to support the theory that polymerization had occurred through the aliphatic portion of the ester. Consistent results were observed for all three ester systems, the following data for the polymer obtained from non-isotopic *iso*propyl benzoate being used as an example of the infra-red experiments.

(a) An appreciable difference was observed in the aliphatic C–H region (2900–3000 cm^{-1}) of the polymer spectrum when compared with the *iso*propyl region of the pure ester. Besides the very strong absorption peak at 2980 cm^{-1} which is characteristic of the *iso*propyl C–H stretching frequency, an additional equally intense peak was observed *only in the polymer* at 2940 cm^{-1}.

(b) The integrated area under the curve for the aliphatic C–H region of the polymer was almost twice the value for the corresponding region in *iso*propyl benzoate.

(c) There was no observable difference in the spectra of the aromatic regions of both polymer and recovered ester. This indicates the absence of substituted benzoates formed by radical attack on the benzoic acid portion of *iso*propyl benzoate.

Hydrolysis of polymers

Conventional alkaline hydrolysis performed on each polymer yielded pure benzoic acid, and a polymeric fraction which possessed an infra-red spectrum, exclusively aliphatic in nature but quite different from the reference spectrum of *iso*propanol. There was evidence of appreciable changes in the C–H, C–D and O–H stretching bands from those of the parent *iso*propanols. The specific activity of this polymeric aliphatic material was several-fold greater than the specific activity of the aliphatic portion of the corresponding ester, whereas there was very little difference in the comparative activities of the benzoic acids derived from polymer and recovered ester.

Hydrolysis of iso*propyl benzoates*

A mixture of 1·0 g ester, 3·0 ml diethylene glycol, 9·0 ml water and 0·6 g potassium hydroxide contained in a microdistillation flask with side-arm condenser, was heated slowly under nitrogen† to 100°C until homogeneous, then cooled to 80°C and the *iso*propyl alcohol slowly distilled through the side-arm condenser. The stillpot residue was diluted with 6·0 ml water and acidified with 20% sulfuric acid. Benzoic acid (0·76 g) thus obtained was purified by recrystallization from 25% aqueous methanol. The specific activities of the benzoic acids obtained from each of the three esters are shown in Table 1.

The distillate containing *iso*propanol was divided into two equal portions, one for derivatization as the 3,5-dinitrobenzoate, the other for oxidation to acetone. An infra-red spectrum of the alcohol at this point indicated that no carbonyl material (from autoxidation of the glycol) was present in the distillate.

Iso*propyl*-3,5-*dinitrobenzoate* was prepared from *iso*propanol and 3,5-dinitrobenzoyl chloride. It was purified by recrystallization from 50% aqueous alcohol. m.p. 121–2°C. Mixed melting point showed no depression. The specific activity after each recrystallization is listed in Table 2.

Acetone-2,4-*dinitrophenylhydrazone*. *Iso*propanol (100 mg) was oxidized in a sealed

* All spectra were recorded on a Perkin–Elmer Model 21 instrument.

† Autoxidation of the diethylene glycol was kept to a minimum by performing the hydrolysis under nitrogen.

TABLE 1. Specific activity of benzoic acids from irradiated esters

Recrystallization number	Acid from *iso*propyl benzoate		Acid from *iso*propyl-d_6 benzoate		Acid from *iso*propyl benzoate-d_5	
	μc/mg	μc/mmole	μc/mg	μc/mmole	μc/mg	μc/mmole
1st	0·156	19·0	0·172	21·0	0·155	19·6
2nd	0·155	18·9	0·169	20·6	0·150	19·0
3rd	0·154	18·8	0·169	20·6	0·149	18·9

TABLE 2. Specific activity of alcohol derivatives after recrystallization

Recrystallization	*Iso*propyl-3,5-dinitrobenzoate from *iso*propyl benzoate		Acetone-2,4-D.P.H. from *iso*propyl benzoate		Acetone-2,4-D.P.H. from *iso*propyl-d_6 benzoate		Acetone-2,4-D.P.H. from *iso*propyl benzoate-d_5	
	μc/mg	μc/mmole	μc/mg	μc/mmole	μc/mg	μc/mmole	μc/mg	μc/mmole
1st	0·0409	10·4	0·0360	8·57			0·0415	9·91
2nd	0·0406	10·3	0·0359	8·55	0·0277	6·77	0·0415	9·91
3rd	0·0406	10·3	0·0357	8·50	0·0270	6·60	0·0414	9·89
4th					0·0268	6·55		

flask by 330 mg potassium permanganate contained in 15 ml water in the presence of 330 mg magnesium sulfate as buffer at room temperature for 20 hr. The acetone was pumped off and collected in liquid nitrogen traps which were washed out with 4 × 5 ml aliquots of water and the washings added drop-wise to a chilled saturated solution of 2,4-dinitro-phenylhydrazine in 2 N hydrochloric acid (250 ml). The mixture stood at 0°C for 1 hr, was filtered, the precipitate washed successively with 2 N hydrochloric acid, and water, then recrystallized from methanol. m.p. 125–6°C. The specific activity after each recrystallization is shown in Table 2.

RESULTS AND DISCUSSION

A summary of the results of the three *iso*propyl benzoate irradiations is outlined in Table 3.

Using the data reported in Tables 1, 2 and 3, the distribution of tritium in each of the three labelled ester systems has been calculated and summarized in Table 4.

The results obtained for the distribution of tritium in *iso*propyl benzoate (non-deuterated), showing a preference for ring

TABLE 3. *Iso*propyl benzoate irradiations

Mixture irradiated	*Iso*propyl benzoate	*Iso*propyl-d_6 benzoate	*Iso*propyl benzoate-d_5
	3·6900 g ester 0·595 g lithium myristate	3·0530 g ester 0·529 g lithium myristate	3·256 g ester 0·514 g lithium myristate
Time of irradiation (hr)	118	128	153
Flux[a] (n/cm²/sec)	$1·0 \times 10^{21}$	$1·0 \times 10^{12}$	$1·0 \times 10^{12}$
Calculated T activity (μ)	2220	2110	2450
Recovered ester specific activity (μc/mg)	0·188	0·187	0·217
Lithium myristate specific activity (μc/mg)	0·200[b]	0·159[b]	0·181[b]
Polymer[c] specific activity (μc/mg)	1·096	0·549	0·562
Recovered ester total activity (μ)	377 (16·8%)[d]	402 (19·0%)[d]	250 (10·2%)[d]
Polymer[c] total activity (μ)	657 (29·3%)[d]	467 (22·1%)[d]	562 (22·9%)[d]
Gas activity (μc)	750 (33·4%)[d]	625 (29·6%)[d]	1040 (42·2%)[d]
Volume s.t.p. (cm³)	137·2	100·7	138·5
Pressure (cm)	237·9	210·8	311·4

[a] Flux is accurate to 10 per cent.
[b] These figures were not constant after four recrystallizations. The drop in specific activity between the third and fourth recrystallizations was still appreciable.
[c] Non-distillable oil remaining after recovery of lithium myristate and *iso*propyl benzoate from the mixture after irradiation.
[d] Percentage figures based on calculated T activity.

TABLE 4. Tritium distribution in the esters

Compound irradiated	*Iso*propyl benzoate	*Iso*propyl-d_6 benzoate	*Iso*propyl benzoate-d_5
Hydrolysis product	Activity μc/mmole	Activity μc/mmole	Activity μc/mmole
Benzoic acid	18·8	20·6	18·9
Acetone-2,4-dinitrophenylhydrazone	8·50	6·55	9·89
*Iso*propyl-3,5-dinitrobenzoate	10·3		
Relative activity per CH			
Aryl	2·66 ± 0·05	3·78	2·30
Primary aliphatic	1·00	1·00	1·00
Secondary aliphatic	1·28[a] ± 0·10		

[a] This figure has been derived by difference whereas other data have been computed from direct measurements.

tritiation over methyl group tritiation by a factor of 2·66 (per C–H), add to the growing body of such data.* An effect in this direction was observed by KAPLAN[9] in the labelling of toluene. Within the *iso*propyl group, our results suggest a slight preference for tritiation on C–2 as compared with C–1 by a factor of 1·3, but the difference is not large in relation to the uncertainty resulting from the fact that the activity at C–2 is obtained by difference.

The H/D isotope effect is evaluated by noting that the ratio 2·66 for the ratio of tritium substitution at a ring position to substitution at a methyl group position in *iso*propyl benzoate, shifts to 3·78 in *iso*propyl-d_6 benzoate. If it is assumed that the extent of ring tritiation is not influenced by the isotopic composition of the *iso*propyl group and therefore can be used as an internal standard, the H/D isotope effect for tritiation at a methyl group is given as 3·78/2·66, or 1·41. Similarly, the H/D isotope effect for ring tritiation (averaged over all ring positions) is written as 2·66/2·30, or 1·16, again with an assumption, namely, that the presence of deuterium in the ring does not influence tritiation in the methyl groups.

These assumptions appear to be reasonable in the present state of knowledge concerning radiolytic processes. Consequently, it is believed that there is a significant, though not large, H/D isotope effect in the primary tritiation process taking place on an alkyl carbon atom and a smaller effect, if any, in ring tritiation. This conclusion suggests that there is a significant mechanistic difference in the two cases and that the tritium substitution on an aromatic ring occurs by tritium capture, followed by the expulsion of hydrogen as a later event, whereas in substitution on a saturated carbon atom, the initial event is accompanied by C–H bond weakening.

To this is added a word of caution against interpreting the tritium distribution ratios (showing preponderant ring tritiation) as reflecting the rates of attack at ring positions relative to attack in the alkyl group. These ratios show only the relative frequencies of those events in which the target molecule survives having suffered only replacement of H by T. The fact that a greater number of events occurs in the alkyl group with retention of tritium but with chemical consequences such that polymeric materials are formed, is shown by distribution studies with the labelled polymeric by-products. On a comparative basis, a much larger incorporation of tritium occurs in the aliphatic portion of the polymer than in the corresponding alkyl group of the recovered ester. This is in marked contrast to the very small differences in tritium activity observed for the aromatic portions of both polymer and recovered ester. All three ester systems, namely *iso*propyl benzoate, *iso*propyl-d_6 benzoate and *iso*propyl benzoate-d_5 yielded consistent results in this respect.

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* We have also observed[8] in neutron–irradiation of powdered mixtures of lithium oxalate with d(+)-2-octyl phthalate, and with l(−)-2-octyl phthalate, that tritiation in ring positions is found to a greater extent than tritiation in the octyl group by factors (calculated per C—H) of 3·0 and 3·3 for duplicate irradiations.

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Stress–Strain Properties of Irradiated Filled Natural Rubber

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The stress–strain behaviour of carbon-black filled natural rubbers cured by exposure to 2 MeV electrons has been examined in relation to that of normal vulcanizates. A simple empirical power law relating modulus to elongation has facilitated handling of the experimental data. Antioxidants and other normal ingredients of the rubber mix confer improved ageing resistance but also increase the radiation dose required for a given modulus.

Comparing radiation and sulphur cure, the former gives products adequate in modulus and ageing resistance but inferior in ultimate elongation for a given modulus and in tensile product. Special formulation may lead to improved products.

LES PROPRIÉTÉS APPUI-DÉFORMATION DU CAOUTCHOUC NATUREL CHARGÉ APRÈS IRRADIATION

Le comportement en rapport d'appui-déformation des caoutchoucs maturels chargés de noir de carbone, traités avec des électrons de 2 MeV a été soumis à l'examen vis-à-vis celui des caoutchoucs vulcanisés normalement. Une loi de puissance simple et empirique pour le rapport entre le module et l'allongement a rendu plus facile la manipulation des données expérimentales. Les antioxydisants et les autres ingrédients normaux du mélange de caoutchouc donnent une résistance supérieure au vieillissement mais augmentent aussi la dose de radiation necessaire pour un module donné.

Pour comparer le traitement à la radiation et au soufre: le premier donne des produits de module et de résistance au vieillissement suffisants, mais d'allongement ultime pour un module donné et de produit de tension inférieurs. Une formulation spéciale pourrait mener à des produits améliorés.

ДЕФОРМИРУЮЩИЕ СВОЙСТВА ОБЛУЧЕННОГО НАПОЛНЕННОГО НАТУРАЛЬНОГО КАУЧУКА

Зависимость деформации от напряжения для натурального наполненного угольной сажей каучука, облученного электронами с энергией 2 Мэв, определялась по отношению к нормальным вулканизатам. Обработка экспериментальных данных облегчается применением простого эмпирического степенного закона, связывающего модуль с растяжением. Антиоксиданты и другие нормальные ингредиенты резиновой смеси улучшают сопротивление старению, но требуют увеличения дозы облучения для денного модуля.

Сравнение радиационной и серной вулканизации показывает, что первая дает продукты, равноценные по модулю и сопротивлению старению, но худшие в отношении предельного растяжения при данном модуле и обладающие меньшим сопротивлением разрыву.

DIE ELASTISCHEN EIGENSCHAFTEN VON BESTRAHLTEM, MIT EINBETTMITTELN VERSEHENEM NATURGUMMI

Die elastischen Eigenschaften von russ-beschwertem Naturgummi nach Ausheilung durch Bestrahlung mit 2 MeV-Elektronen wurde untersucht und mit normalen Vulkanisaten verglichen. Ein einfaches, empirisches Kraftgesetz, welches Modul und Dehnung in Relation setzt, half dabei die experimentellen Daten zu verarbeiten. Oxydationshemmende Mittel und

andere normale Bestandteile der Gummimischung bewirken einen verbesserten Widerstand gegenüber Alterung, steigern aber auch gleichzeitig die bei gegebenem Modul erforderliche Strahlendosis.

Bei Vergleich der Ausheilung durch Bestrahlung oder durch Verwendung von Schwefel ergibt ersteres geeignete Produkte bezüglich Modul und Widerstand gegenüber Alterung, die jedoch bezüglich Streckgrenze und Spannungsprodukt unterlegen sind.

Spezielle Zusammensetzung mag zu verbesserten Produkten führen.

INTRODUCTION

PUBLISHED work on the irradiation of rubber has been concerned on the one hand with evaluating the resistance of conventionally-vulcanized rubber stocks to radiation damage,[1–3] and on the other, with effecting cure of raw elastomers without the use of sulphur and similar vulcanizing ingredients.[4–6] The effect of ionizing radiation on natural rubber vulcanizates is to increase modulus and to reduce tensile strength, elongation and flex resistance:[7] however, it is classed as one of the more resistant organic compounds.

The effect of radiation on unvulcanized stock is to reproduce the mechanical properties of the sulphur-cured material: the doses required are, however, relatively high. The question arises as to the point at which the radiation ceases to be beneficial and becomes damaging and whether it is indeed possible to separate the two effects.

Without overlooking the degradative action of the irradiation treatment, this paper is primarily concerned with the *beneficial* aspects of radiation, namely its alleged capacity to compete with chemical-cure. Particular attention is given to the resistance of radiation-cured stocks to deterioration during subsequent heat ageing. It has been claimed that even without antioxidants, radiation vulcanized rubber has greater resistance to ageing than conventional rubber containing antioxidants.[8,9] It has further been stated that the usual chemical agents present in vulcanized rubber do not have much effect, but that irradiation in the presence of oxygen is very degrading.[10]

Most reported studies on radiation-cured rubber have used a pure gum stock, for obvious reasons. CHARLESBY *et al.* more recently, however, have considered the influence of carbon black on mechanical properties and have suggested an empirical method of characterizing rubber stocks in terms of a single stress–strain parameter.[11] This paper may be regarded as an extension of the earlier work, though some modification of the previous analysis has been necessary.

ANALYSIS OF STRESS–STRAIN DATA

The statistical theory of rubber-like elasticity predicts the relationship[12]

$$L = \frac{RT\rho}{M_c}\left(\alpha - \frac{1}{\alpha^2}\right) \qquad (1)$$

where L is the stress based on original cross sectional area, α is the ratio of extended to initial length, ρ is the density of the rubber and M_c the average molecular weight between junction points. This purely statistical treatment holds surprisingly well for vulcanized natural latex:[13] obvious deviations can be theoretically accounted for. However, it breaks down completely for reinforced stocks. One weakness of the statistical theory is that it does not consider the nature of the cross-link, but assumes it to be inter-changeable with main chain links. Naturally, it cannot account for effects due to crystallization or due to any delayed response to internal stresses.

Better agreement still for gum stocks arises if the load at a given extension is plotted against $1/M_c$.[14] Thus the elastic modulus provides a useful measure of the degree of cross-linking, due allowance being made for free chain ends. In the case of irradiated gum stocks, crystallization effects seem less dominant and CHARLESBY and VON ARNIM[15] found a linear relationship

between load and the function $(\alpha - 1/\alpha^2)$, in direct confirmation of the statistical theory.

An alternative approach to analysis of the stress–strain curve, in cases where equation (1) does not apply, makes use of the Nutting equation. This can be written in the form

$$L^m = Kxt^p \qquad (2)$$

where x is the extension $(\alpha - 1)$, t is the time and K, m, p, are arbitrary constants. Introducing the constant rate of extension $R = x/t$, this can be rearranged to

$$L = K^{1/m}\, x^{(1+p)/m}\, R^{-p/m} = fx^n \qquad (3)$$

where $n = (1+p)/m$ and $f = L_{(x=1)} = (K/R^p)^{1/m}$

The power law of equation (3) implies that straight lines of slope n will arise if the load is plotted against extension on log-log paper. For tests at constant strain rate, this linear relationship has indeed been observed for plasticized polyvinyl chloride up to extensions of 30 per cent, with values of n between 0·5 and 1·0.[16] As will be seen, equation (3) also fits most of the present stress–strain data on carbon-black loaded cross-linked rubbers, agreement being best at high extensions (100–500 per cent).

In an earlier study of the applicability of equation (3) to carbon-black loaded irradiated rubbers, the exponent n was found to be nearly equal to 2 for all the compositions studied, at least at high extensions. This encouraged analysis of the data in terms of the expression

$$L = (Fx)^2 \qquad (4)$$

where F was now a dose-independent parameter completely specifying the stress–strain properties of the particular mix.[11]

More detailed work, presented here, has shown that the constancy of the exponent n cannot be sustained. It varies, in fact, between the extremes 1·1–2·3. Accordingly, both f and n parameters are necessary to completely specify the stress–strain properties and it has been preferred to discard the earlier F values and re-analyse the dependence between f and the radiation dose r.

Although the proportionality constant f is shown above, in terms of the Nutting equation, to be a complex function of the strain rate, it must be recognized that under a fixed strain rate, f is nothing more than the 100 per cent modulus. It differs only from the observed 100 per cent modulus, insofar as the extrapolated value reflects contributions from observed moduli at higher extensions. It is thus characteristic of the whole stress–strain curve and might be regarded as a "weighted" 100 per cent modulus.

Assuming random cross-linking by radiation, it is reasonable to expect a linear relationship between the elastic modulus E and the radiation dose r. A relationship of the type

$$E = a + br \qquad (5)$$

was indeed observed for pile-irradiated natural rubber,[6] the small intercept being attributed to chain entanglements. It is considered justifiable to substitute f for E, leading to

$$f = a + br \qquad (6)$$

Converting the intercept observed by CHARLESBY and GROVES[6] to the units employed in this work, one gets the value $a = 23$ lb/in^2. In plotting f against r for compositions studied in the present work, analysis of "best" straight lines by the least squares method leads to values of a varying from $+30$ to -30 lb/in^2. These values are always small in comparison with the second term br, and lack statistical significance. We have therefore taken it to be zero, as in the earlier work,[11] with a view to simplifying subsequent analysis.

Contrary to earlier reports,[10,11] we have found evidence of "protective action" by antioxidants and other ingredients of the conventional rubber formulation. Radiation protection effects are normally of two types, additive or proportional. Additive protection implies a certain energy input to be expended without producing change to the substrate, whereas proportional protection implies immediate changes in the substrate, but at a lower rate of efficiency. These effects correspond to inhibition and retardation in polymerization systems. Additive

protection in the present case would shift the f versus r curves to the right, (see Fig. 6) but maintain their slopes, while pure proportional protection would maintain the intercept but change the slope. A combination of additive and proportional protection (which occurs quite frequently) would change both slope and intercept. While the results to be reported are too diffuse to rule out a small additive component, it is clear from Fig. 6 that the protection is largely proportional, i.e.

$$f = \frac{br}{c} \qquad (7)$$

where c is a characteristic factor whose reciprocal is a measure of the efficiency of the radiation. The value of c may be used to calculate a "protection coefficient"[17] which is equal to $(1 - 1/c)$.

The ultimate elongation e was always found to be very sensitive to dose. An exponential relationship between elongation and dose was previously observed.[11] Only partial support for this relationship arises from the present sets of results: deviations frequently occur in the high dose range. If attention is confined to the low dose range (up to 10^8 rad), then the linear relationship of equation (8) holds at least as well and this form has been used for the purpose of discussion.

$$e = p - qr \qquad (8)$$

The combination of equations (7) and (8) leads to values of the maximum tensile strength, as will be seen below.

Another parameter observed to vary markedly with the composition and type of cure was the tensile product, that is to say, the ultimate tensile stress based on the cross-sectional area at break. Values of the tensile product were calculated from the maximum tensile stress and the elongation at break, assuming constancy of volume of sample. These corroborated certain conclusions relating to protective action.

EXPERIMENTAL

Rubber samples in the form of pressed sheets 3 mm thick containing carbon-black and various additives were prepared in the laboratories of Cabot Carbon Ltd, Ellesmere Port, Cheshire. The standard formulation used for chemical cure was: blended smoked sheet, 100; carbon-black, variable; zinc oxide, 5; stearic acid, 3; Tackol, 3·5; Nonox HFN, 1; sulphur, 2·5; Santocure, 0·5.

In contrast, for many radiation cures, only the binary mixture of blended smoked sheet and carbon-black was used. Irradiations were also conducted, however, on more complex mixtures as indicated below.

Radiation cures were performed in all cases at normal room temperature using electrons generated by the 2 MeV Van de Graaff accelerator at Hinxton Hall, Cambridge. The radiation doses were absorbed in units of 1 Mrad, delivered in 1 sec, with the sample supported on a conveyor belt passing below the beam. Suitable intervals between passes prevented excessive temperature rise. Irradiations were performed in a normal atmosphere, on the view that the oxygen initially contained in the specimens would be removed in the first pass and that replenishment of oxygen in the bulk of the sample would not be possible during the time scale of the experiment.

From both irradiated and chemically cured sheet, dumb-bells were cut and tested, before and after ageing, on the Cabot Carbon rubber tensile testing machine at a cross-head speed of 20 in/min. Several samples were tested per sheet and figures used in this paper are average values of modulus, tensile strength and elongation. The ageing period was 14 days at 70°C in air at normal pressure.

RESULTS

The following series of experiments were carried out:

Series A. Conventional sulphur cure using the above standard formulation and the following grades and proportions of carbon-black: Sterling FT, 25, 50 and 75 phr; Sterling V, 50 phr; Vulcan 3, 50 phr; Vulcan 6, 25, 50 and 75 phr; Spheron 9, 50 phr.

Series B. Conventional sulphur cure of the

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standard formulation with 50 phr Vulcan 6, but with varying cure times.

Series C. Radiation cure using binary mixtures of blended smoked sheet with the same grades and quantities of carbon-black listed in Series A.

Series D. Radiation cure using a mixture of blended smoked sheet with 50 phr Vulcan 6, and, in addition, 1 phr of one of the following antioxidants: Nonox HFN, PBN, Nonox EX, Flectol H, Nonox CI, Santowhite crystals, UOP 88 (an antiozonant used at 2·5 phr level).

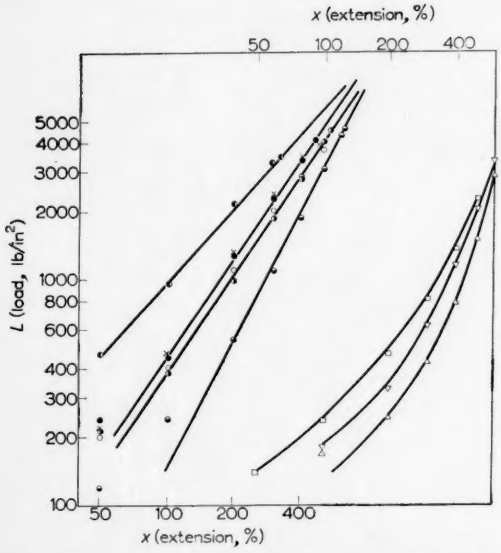

FIG. 1. Stress–strain curves for conventionally sulphur-cured carbon-black filled natural rubber sheets. ● Vulcan 6, 50 phr; × Vulcan 3, 50 phr; ○ Sterling V, 50 phr; ◑ Spheron 9, 50 phr; ◐ Vulcan 6, 75 phr; ◒ Vulcan 6, 25 phr; Δ Sterling FT, 25 phr; ▽ Sterling FT, 50 phr; □ Sterling FT, 75 phr.

Series E. Radiation cure using the standard formulation with 50 phr Vulcan 6 but without the sulphur.

Series F. Radiation cure of the standard formulation with 50 phr Vulcan 6 which has been partially pre-cured by heat.

Stress–strain curves (Series A & C)

The stress–strain results for the conventionally sulphur-cured rubbers are plotted logarithmically in Fig. 1. Straight lines can be drawn through all the points for the 75 phr Vulcan 6 formula, through the points for 100 per cent extension and greater for the four 50 phr formulae and through the points for 200 per cent extension and over for the 20 phr Vulcan 6 formula.

TABLE 1. Parameters for sulphur-cured rubbers containing various carbon-blacks

		f	n
Vulcan 6,	75 phr	960	1·1
Vulcan 6 / Vulcan 3	50 phr	460	1·45
Sterling V / Spheron 9	50 phr	400	1·45
Vulcan 6	25 phr	150	1·9

The empirical parameters for these straight lines are given in Table 1.

On the other hand, the large particle size black Sterling FT gives results which, as shown on the right hand side of Fig. 1, defy the logarithmic relationship of equation (3) and no further analysis can be attempted for

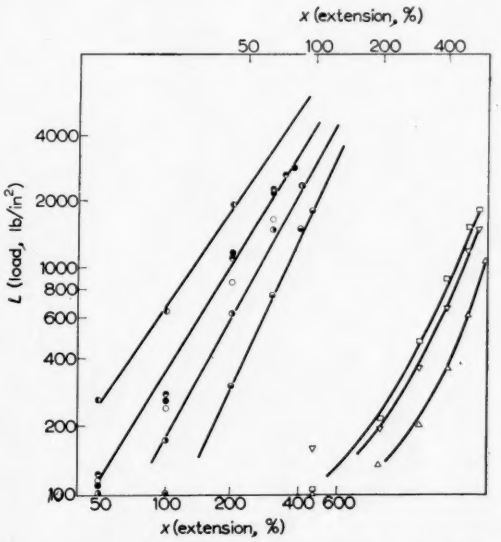

FIG. 2. Stress–strain curves for 40 Mrad radiation-cured carbon-black filled natural rubber sheets. ● Vulcan 6, 50 phr; ◓ Vulcan 3, 50 phr; ○ Sterling V, 50 phr; ◑ Spheron 9, 50 phr; ◐ Vulcan 6, 75 phr; ◒ Vulcan 6, 25 phr; Δ Sterling FT, 25 phr; ▽ Sterling FT, 50 phr; □ Sterling FT, 75 phr.

Table 2. Parameters for radiation-cured rubbers containing various carbon-blacks (40 Mrad)

		f	n
Vulcan 6	75 phr	670	1·48
Vulcan 6 / Vulcan 3	50 phr	340	1·62
Sterling V	50 phr	230	1·78
Spheron 9	50 phr	170	1·84
Vulcan 6	25 phr	62	2·3

this type of composition. CHARLESBY *et al.*[11] found similar curvilinear logarithmic plots for unfilled irradiated rubber.

Similar sets of curves are shown in Fig. 2 for the rubber sheets of series C irradiated to the 40 Mrad level only. The empirical parameters for the straight lines on the left of this figure are given in Table 2.

On the right hand side of Fig. 2 are shown results for the three formulations containing Sterling FT. Although curved lines are shown drawn through these points, it is also possible to draw straight lines through the points for extensions of 200 per cent or over. These straight lines would have slopes in excess of 2; i.e. 2·1, 2·3 and 2·6 for 75 phr, 50 phr and 25 phr respectively.

TABLE 3. Parameters for sulphur-cured rubbers as a function of cure time

Time of cure at 280°F (min)	Normal specimens			Aged specimens		
	f	n	e	f	n	e
10	90	1·88	580	230	1·56	580
20	230	1·68	570	500	1·28	490
40	440	1·45	520	660	1·28	410
60	440	1·45	490	660	1·28	360
80	440	1·45	480	660	1·28	380

Varying cure time (Series B)

The standard composition with 50 phr Vulcan 6 was mechanically tested after curing in a press at 280°F for 10, 20, 40, 60, 80 min respectively. The compounds were again tested after ageing. The logarithmic stress–strain curves appear in Fig. 3. The parameters derived from these curves are given in Table 3, which also includes the ultimate elongation e. It is seen that no further increase in f and no further decrease in n occurs after 40 min cure time. Overcure leads to a small further reduction in ultimate elongation, however.

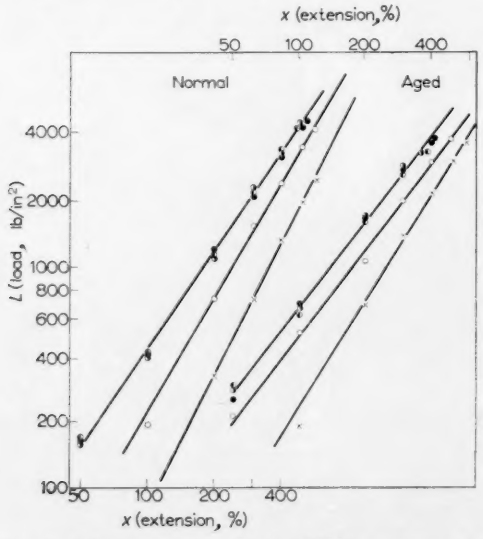

FIG. 3. Influence of cure time at 280°F on stress–strain curves. × 10 min cure; ○ 20 min cure; ● 40 min cure; ◑ 60 min cure; ◐ 80 min cure.

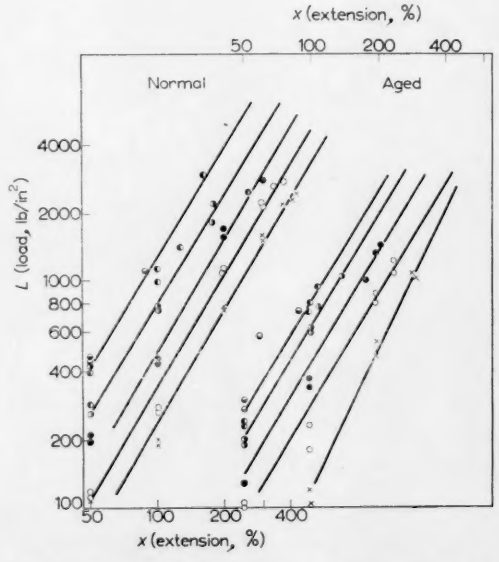

FIG. 4. Influence of radiation dose on stress–strain curves. × 25 Mrad; ○ 40 Mrad; ● 60 Mrad; ◑ 90 Mrad; ◐ 120 Mrad; ◒ 150 Mrad.

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Varying radiation doses (Series C)

The influence of radiation dose was examined by analysing the stress–strain data for two formulations, selected from Series C, which had been irradiated with doses up to 150 Mrad. Vulcan 6 and Vulcan 3 gave closely similar values and the results have been combined in the logarithmic stress–strain curves for both normal and heat-aged material shown in Fig. 4. The parameters obtained are shown in Table 4, which includes ultimate elongation values for the mix containing Vulcan 6 only. A progressive increase in f with dose is seen to occur, but there is little variation in n.

TABLE 4. Parameters for radiation-cured rubbers as a function of dose

Radiation dose (Mrad)	Normal specimens f	n	e	Aged specimens f	n	e
25	230	1·66	420	120	2·1	290
40	340	1·66	370	280	1·64	240
60	480	1·66	300	430	1·62	210
90	800	1·60	180	600	1·64	140
120			160			110
150	1300	1·60	90	800	1·60	60

Various antioxidants (Series D)

The reduction in modulus following heat-ageing which is apparent from Table 4 was tentatively attributed to oxidation of the cross-linked rubber. To test this hypothesis and with a view to producing more satisfactory ageing properties, various antioxidants were incorporated together with 50 phr Vulcan 6 into the blended smoked sheet and the stress–strain curves were determined before and after ageing following radiation doses of 25, 40 and 60 Mrad respectively. The usual linear plots were obtained on double logarithmic paper. The results on the aged specimens were sufficiently close in most cases to allow a single line through the points for a given dose. This has been done for the composition containing 1 phr Nonox HFN, shown in Fig. 5. The parameters obtained are shown in Table 5, and may be compared with those in Table 4 for antioxidant-free rubbers.

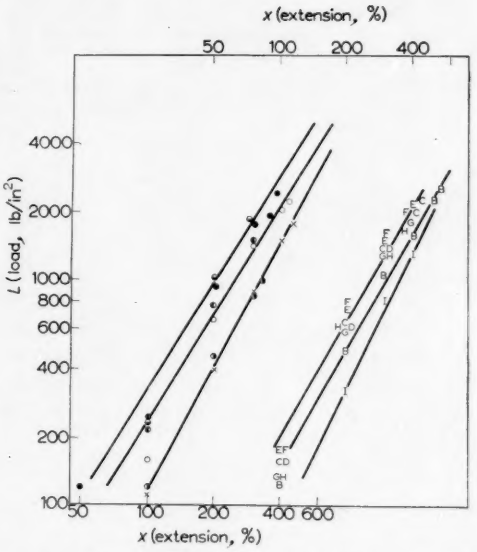

FIG. 5. Influence of antioxidants on stress–strain curves. × 25 Mrad normal; ○ 40 Mrad normal; ● 60 Mrad normal; ◑ 25 Mrad aged; ◐ 40 Mrad aged; ◒ 60 Mrad aged; B Full formula; C Nonox HFN; D PBN; E Nonox EX; F Flectol H; G Nonox CI; H Santowhite crystals; I UOP 88.

On the right hand side of Fig. 5 are plotted results obtained with different antioxidants for a common dose of 40 Mrad from which it may be seen that Nonox CI (G) has the greatest protective power, while Flectol H (F) has the smallest protective power. Still further protection arises with the other normal ingredients as shown by the location of the line passing through the points B which relate to the formulation of series E (standard formulation less sulphur). The greatest protective action of all occurs with the antiozonant UOP 88. This may be due to the higher concentration added, namely 2·5 phr. All the additives protect also against

TABLE 5. Parameters for radiation-cured rubbers containing Nonox HFN

Radiation dose (Mrad)	f	n	e normal	e aged
25	120	1·84	450	330
40	230	1·60	430	360
60	330	1·60	380	290

TABLE 6. Parameters for radiation-cured rubbers containing all normal ingredients less sulphur

Radiation dose (Mrad)	Normal f	n	e	Aged specimens f	n	e
25	110	1·77	570	120	1·67	410
40	150	1·74	530	180	1·65	430
60	210	1·67	460	220	1·64	420

degradation during ageing to a greater or lesser degree and from this standpoint the results with Nonox HFN may be regarded as representative. The parameters characterizing the best line passing through the points for all the antioxidants are $f = 200$, $n = 1{\cdot}72$ while for the antiozonant $f = 70$, $n = 2{\cdot}1$.

Full vulcanization formula (Series E)

The suspicion that the normal ingredients of the conventional rubber mix have protective action led to the measurement of stress–strain properties for the irradiated sheets of series E. The usual linear plots were obtained, one of which (B points) appears in Fig. 5. The parameters obtained are given in Table 6 (compare Tables 4 and 5).

It is seen from Table 6 that, in common with the simpler mixes containing antioxidants only, ageing produces only minor changes in f and n values, and that the chief effect of ageing is to reduce elongation.

Irradiation plus thermal pre-cure (Series F)

The final series of measurements was concerned with the possibility that thermally undercured rubber sheet might be brought to full cure by subsequent irradiation. To this end, the stress–strain curves were analysed for sheets subject to 25, 40, 60 Mrad following a 10 min (280°F) pre-cure in a press. The parameters are shown in Table 7.

By comparing this table with Table 3, it is evident that radiation can advance the cure to give much the same stress–strain curve as for the fully-cured rubber. It may also be noted that the samples harden on ageing in the same way as the heat cured material. This increase in modulus on ageing is seen to arise only in the presence of sulphur.

TABLE 7. Parameters for thermally-undercured rubber, subsequently irradiated

Radiation dose (Mrad)	Normal f	n	e	Aged specimens f	n	e
0	90	1·88	580	230	1·56	580
25	230	1·58	570	420	1·37	—
40	270	1·58	490	420	1·37	490
60	360	1·50	440	420	1·37	480

Protective action

The observed variation in f values at the same irradiation level for different mixes signifies the existence of protective effects. In Fig. 6, the f values for various mixes are plotted against radiation dose. A linear relationship appears to be followed. It is not possible to measure the f value directly for the unvulcanized, unirradiated mix because the logarithmic relationship between L and x is not obeyed. In theory however, the f value for the uncross-linked rubber

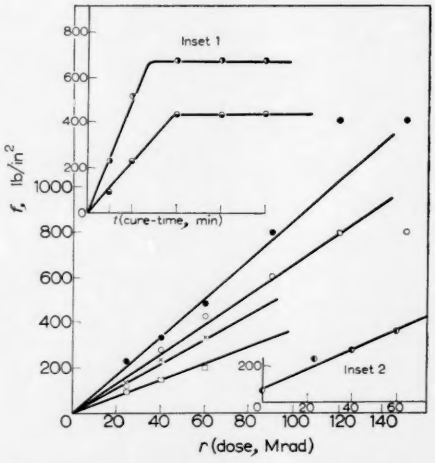

FIG. 6. Dependence of f values on radiation dose and (inset) on cure time. ● Rubber + 50 phr Vulcan 6—normal specimens; ○ rubber + 50 phr Vulcan 6—aged specimens; × specimens containing 1 phr Nonox HFN; □ specimens containing all ingredients for conventional vulcanization less sulphur.
Inset 1. ◒ Conventional vulcanizate—normal samples; ◑ aged samples.
Inset 2. ◐ Conventionally vulcanized for 10 min followed by irradiation.

TABLE 8. Dependence of f values on radiation dose r

Description	Additive	Slope	Efficiency factor (%) $(1/c)$	Protection coefficient (%) $(1-1/c)$
Series C, normal	Nil	8·6	100	0
Series C, aged	Nil	6·6	(77)	(23)
Series D, normal and aged	Nonox HFN	5·5	64	36
Series E, normal	All ingredients	3·7	42	58
Series F, normal	All ingredients plus sulphur	4·2	49	51

should be close to zero. The lines of Fig. 6 accordingly have been drawn passing through the origin and the graphically derived slopes have been used to calculate protection coefficients. It is noted from inset 1 on this figure that curves linking f values with cure times during conventional vulcanization are also linear for periods short of complete cure and appear to pass through the origin.

The term "protection coefficient" was defined by ALEXANDER *et al.*[17] as being the quantity $(1 - r'/r)$, where r is the dose given and r' is the dose which would result in the same amount of change in the absence of protective action. In terms of the factor c of equation (7) the protection coefficient is $(1 - 1/c)$. The dependence of the efficiency factor $(1/c)$ and the protection coefficient on the additives present in radiation-cured rubbers is shown in Table 8. When the efficiency factor of series E is calculated relative to series D, it comes to 66 per cent. Thus the additional ingredients in series E have collectively a protective action similar to that of the antioxidant alone. The increased efficiency factor of series F indicates that when some of the sulphur and other ingredients have reacted, the protective power is reduced.

Ultimate elongation

A number of values of ultimate elongation are presented in Fig. 7 as a function of the radiation dose. Up to a dose of 100 Mrad, the results are reasonably represented by straight lines, at least for the unaged specimens. The parameters derived from these curves are shown in Table 9.

The interpretation of the results of Table 9 is rendered uncertain by the absence of any common origin for the straight lines.

A combination of equations (7) and (8)

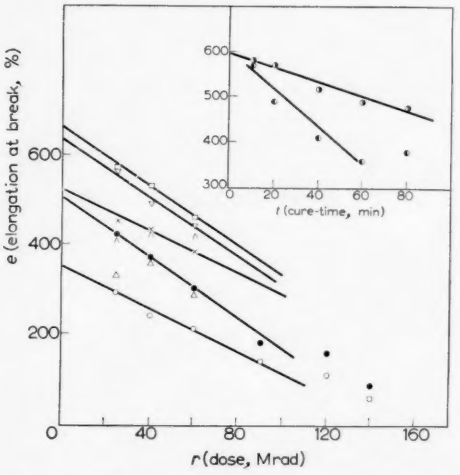

FIG. 7. Dependence of ultimate elongation on radiation dose and (inset) on cure time. ● Rubber + 50 phr Vulcan 6—normal specimens; ○ rubber + 50 phr Vulcan 6—aged specimens; × specimens containing 1 phr Nonox HFN—normal; Δ specimens containing 1 phr Nonox HFN—aged; □ conventional formulation less sulphur—normal; ∧ conventional formulation less sulphur—aged; ∇ conventional formulation with 10 mm pre-cure.

Inset. ◑ Conventional vulcanization—normal samples; ◐ conventional vulcanization—aged specimens.

allows approximate calculation of the ultimate tensile strength of any mix and for any dose given the values of n, b, p and q.

$$T = br(p - qr)^n \qquad (9)$$

If this expression is differentiated and set to zero, one finds a maximum tensile strength arising at the dose given by

$$r = p/qn + q \qquad (10)$$

TABLE 9. Dependence of elongation on dose

Description	Additive	Intercept (p)	Slope (q)
Series C, normal	Nil	500	−3·3
Series C, aged	Nil	300	−2·4
Series D, normal	Nonox HFN	520	−2·4
Series D, aged	Nonox HFN	500?	−3·3?
Series E, normal	All ingredients	660	−3·3
Series F, normal	All ingredients plus sulphur	630	−3·3

TABLE 10. Maximum calculated tensile strengths

Description	Additive	r_{max}	T_{max}
Series C, normal	Nil	57	3000
Series D, normal	All ingredients	60	2000
Series E, normal	All ingredients plus sulphur	74	2000

TABLE 11. Tensile product ($lb/in^2 \times 10^{-3}$) as a function of nature and grade of carbon black and type of cure

Carbon black	phr	Sulphur cure (Series A)	Radiation cure (Series C) 40 Mrad	60 Mrad
Sterling FT	25	27·8	12·1	10·4
	50	25·8	9·8	8·3
	75	20·0	12·0	10·1
Sterling V	50	21·8	11·6	9·9
Vulcan 3	50	22·7	11·5	9·0
Vulcan 6	25	33·4	9·9	9·2
	50	23·0	13·1	11·3
	75	14·3	5·8	4·1
Spheron 9	50	28·8	11·6	10·9

TABLE 12. Tensile product ($lb/in^2 \times 10^{-3}$) as a function of nature of additives and radiation dose

Radiation dose (Mrad)	Series C with 50 phr Vulcan 6	Series D with Nonox HFN	Series E All ingredients	Series F All ingredients plus sulphur
0	—	—	—	16·8
25	10·9	10·0	14·2	23·0
40	13·1	11·7	14·7	18·9
60	11·3	11·7	12·6	15·6
90	6·3	—	—	—
120	5·2	—	—	—
150	2·1	—	—	—

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The maximum tensile strength can accordingly be calculated. Some values appear in Table 10.

Tensile product

It is obvious that a major difference between radiation-cured rubber and sulphur-cured rubber is the smaller elongation at break in the former case. Thus while the f value of a normal vulcanizate can be matched by an irradiated rubber, the elongation in the radiation case for the same f value is lower. This leads to an inferiority in the tensile product as can be seen from Tables 11, 12 and 13.

It is seen from Table 11 that the tensile product varies from 14·3 to 33·4 for sulphur cures depending on the nature and quantity of carbon-black but from 4·1 to 13·1 for radiation cure over the same range, that is to say, the tensile product is reduced by over 50 per cent. Table 12 shows the highest values of tensile product to occur at 40 and 60 Mrad: there is a progressive reduction at higher doses. The presence of antioxidant has little effect but the other normal ingredients of the conventional rubber mix serve to increase the tensile product and a still further increase results when sulphur is present. Table 13 shows that the lowest values of tensile product occur with those antioxidants having the greatest protective power and particularly with the antiozonant UOP 88. It is possible, but unlikely, that higher tensile products would have been observed at higher doses.

TABLE 13. Tensile product ($lb/in^2 \times 10^{-3}$) as a function of nature of antioxidant (Series D)

Antioxidant	25 Mrad	40 Mrad	60 Mrad
Nil	10·9	13·1	11·3
Nonox HFN	10·0	11·7	11·7
PBN	9·6	9·5	10·2
Nonox EX	11·2	10·8	10·4
Flectol H	12·2	9·8	9·6
Nonox CI	10·7	9·1	8·1
Santowhite crystals	7·1	7·9	8·4
UOP 88 (antiozonant)	6·5	6·7	8·4

DISCUSSION

The empirical power law $L = fx^n$ has proven very useful for the interpretation of stress–strain data on carbon-black filled rubbers. This equation applies both to chemical cure and to radiation cure, both f and n being strongly influenced by the nature and proportion of carbon-black. In general, f rises and n decreases with increasing proportion or decreasing particle size of the carbon-black. This is due to the overall hardness and accords with observations on plasticized polyvinyl chloride, where reduced plasticizer content led to increased intercepts and reduced slopes, when the stress–strain data were similarly plotted.[16] For unfilled rubbers and for rubbers filled with coarse thermal blacks, the simple power law does not hold over the whole stress–strain curve.

Comparing chemical cure and radiation cure for a series of identical carbon-black loadings, it is found that radiation cure gives lower f values and higher n values. Certain blacks which give much the same stress–strain behaviour in chemically cured stocks give different parameters in the radiation case. This implies that these blacks have protective power against radiation cross-linking to a varying degree. The protective power of Spheron 9, in particular, seems to be pronounced. It is tempting to attribute this to the origin (channel process) of Spheron 9, but supporting data is necessary. On the other hand, the effects of Vulcan 3 (HAF) and Vulcan 6 (ISAF) seem to be identical and interchangeable. The most striking difference between chemical and radiation cure is the reduced ultimate elongations and, consequently, ultimate tensile strengths and tensile products in the latter case.

For a fixed type and proportion of black (50 phr Vulcan 6), the f value is approximately proportional to the time of cure in the

conventionally vulcanized stocks and to the dose in the radiation case, while the n value remains fairly invariant at approximately 1·6, except for grossly under-cured stocks. Similarly, the ultimate elongations are inversely proportional to the cure time or radiation dose.

Ageing of the rubbers caused changes both in f and n. For sulphur-cured stocks, the f value rises on ageing, but for the radiation-cured material, the f value falls. The elongation e always decreases on ageing, however. Both f and e were found to be approximately proportional to the radiation dose.

The change in f value following ageing can be prevented by incorporation of 1 phr of an antioxidant into the rubber prior to irradiation. In contrast, the elongation is still reduced by ageing. Furthermore, the presence of the antioxidant has a marked protective action on the radiation cross-linking. Thus, the antioxidant-protected formulations, though stable to ageing, start off with inferior modulus properties. A still greater degree of protection both against radiation and ageing emerges when a full vulcanization formula is used. Even though sulphur is absent, the modulus now tends to rise on ageing. The elongation, moreover, of both normal and aged samples is considerably improved.

This increase in elongation is manifest also in the improved tensile product of rubber sheets of series E. The tensile product is more closely linked than any other parameter discussed with the crystallization of the rubber. It is known that several ingredients of a conventional rubber contribute essentially to ease of crystallization. However, with peroxide-cured rubbers, ingredients other than carbon black such as zinc oxide or silica may lead to better properties.[18] Further work will be necessary to establish whether this is true also for radiation-cured rubbers and to identify the component in series E responsible for the improvement.

The major objective stimulating this work has been to ascertain whether special formulation can lead to radiation-cured rubbers with properties equivalent to sulphur-cured material. So far as modulus, or f value, is concerned, this is indeed possible. We have obtained no support for the claim that antioxidant-free irradiated rubbers are more heat-stable than sulphur-cured rubber,[8,9] but this claim was based on stress relaxation studies which have not been made here. In any event, the use of normal antioxidant or, better, the full vulcanization formula confers adequate ageing resistance. Due to the protective action of the ingredients of the mix, the modulus at moderate radiation doses is lower than the equivalent sulphur-cured material but this could presumably be matched by using a higher carbon-black loading. The chief residual drawbacks of radiation-cured rubber are the lower ultimate elongation for a given modulus and the lower degree of crystallization during straining as manifest in the tensile products being reduced by a factor of 50 per cent or more. It is instructive to review suggested reasons for this.

The main hindrance to crystallization is a high degree of cross-linking. According to MORRELL and STERN,[19] the high modulus of a highly cross-linked sample leads to high loads and rupture at low elongations, before the material has become strengthened by crystallization. It is known also that the rate of crystallization decreases sharply with cross-link density. This cannot explain why low-modulus materials do not crystallize, as with peroxide-cure[18] and with the present samples, where the behaviour is closer to that of a non-crystallizing synthetic elastomer. Accordingly, one must attribute the ability to crystallize to the presence of sulphide bonds. These are more easily broken and reformed on straining, suggesting that the ability to yield to the applied stress is essential for crystallization. This is supported by observations on synthetic elastomers containing transient salt linkages, when high tensile products arise.[21] This would imply that the properties of normal vulcanizates can never be reproduced in a carbon–carbon cross-linked material.

Nevertheless there are features in the present study, which are not wholly explained by this picture. In particular, it may be noted that while a certain additive may

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reduce cross-link density and f value, the elongation at break is not correspondingly increased. This leads to the low tensile product values for mixes containing UOP 88, for example. It would appear that there is some additional factor in radiation-cured rubbers responsible for the low elongation at break. The possibility of oxidative degradation during irradiation has been considered. GEHMAN and AUERBACH[10] secured much higher tensile strengths when the γ-irradiated samples were clamped between aluminium plates and sealed to minimize access of oxygen or ozone. We have employed normal atmospheres on the view that diffusion of oxygen would be too slow to affect results, considering the short total duration of the electron irradiation. However, it is still possible that the surface may have become highly oxidized giving rise to surface cracks which subsequently cause premature rupture during the stress–strain test. It is further known that carbon-black may increase the oxidation rate.[20] On the other hand, the tensile strengths obtained in this work are not inferior to those reported by any other workers for radiation-cured rubber, and it is difficult to decide whether this criticism is valid.

Another possible reason for the poorer properties of radiation-cured rubber is the lower temperature of cure. It is known that cold-cured rubbers are inferior to normal vulcanizates. The internal mobility of rubber at room temperature is such that one would not expect any inhomogeneity in the radiation-induced cross-linking action; nevertheless this point may be worth studying in future work. Further useful information would accrue from comparative stress–strain and stress–relaxation measurements with peroxide and sulphur-cured stocks with varying amounts of the cross-linking agent. Reversion and overcure of normal vulcanizates have never been adequately explained, nor has the possibility of structural changes occurring to modify crystallization been thoroughly assessed.

CONCLUSIONS

While the low temperature radiation cure of carbon-black filled natural rubber leads to products with satisfactory modulus, hardness and ageing resistance, they resemble peroxide-cured rubber or vulcanized non-crystallizable synthetic elastomers rather than vulcanized natural rubber. Additives are necessary to confer ageing resistance but these also have protective action and increase radiation dose requirements, which would have to be compensated by an increase in carbon-black content. Radiation-cured sheets have a lower ultimate elongation at a given modulus than the normal vulcanizates and the tensile products are lower by 50 per cent or more. Further work is necessary to establish whether by special formulation the properties of normal vulcanizates can ever be fully matched by radiation cure, in which connexion the type of analysis of stress–strain data used here may be helpful and greater knowledge of the fundamental response of polymers to radiation imperative.

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Mesure Continue d'un Flux de Neutrons par Activation de Solutions en Circulation

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(*Received* 1 *August* 1958)

Les auteurs exposent une méthode de mesure continue d'un flux de neutrons par comptage de l'activité induite dans une solution en circulation dans une tuyauterie souple, ce qui permet de réaliser un détecteur de forme quelconque.

Le choix du corps activé en fonction du but poursuivi est discuté.

CONTINUOUS MEASUREMENT OF A NEUTRON FLUX BY ACTIVATION OF CIRCULATING SOLUTIONS

The authors set out a method for continuously measuring a neutron flux by counting the activity induced in a solution circulating in a flexible loop, which allows the detector to assume any given shape.

The choice of activated material in terms of the aim it must serve is discussed.

СПЛОШНЫЕ ИЗМЕРЕНИЯ НЕЙТРОННОГО ПОТОКА ПУТЕМ АКТИВАЦИИ ЦИРКУЛЯЦИОННОГО РАСТВОРА

Авторами описан метод для сплошного измерения нейтронного потока путем исчисления активации вызванной в растворе циркулирующем в гибком шлейфе, который позволяет детектору принимать любую форму.

Обсуждался выбор активируемого материала, который дложен соответствовать цели, которой он будет служить.

KONTINUIERLICHE NEUTRONENFLUXMESSUNG DURCH AKTIVIERUNG VON ZIRKULIERENDEN LÖSUNGEN

Von den Autoren wird eine Methode vorgeschlagen, durch welche ein Neutronenflux durch die durch ihn induzierte Aktivität einer in einem biegsamen Röhrensystem zirkulierenden Lösung gemessen wird und die die Verwendung beliebiger Detektoren gestattet.

Die Auswahl der für den vorliegenden Zweck am besten geeigneten aktivierten Substanz wird besprochen.

PRINCIPE DE LA MESURE

La mesure d'un flux de neutrons constant par activation d'un détecteur et par comptage de la radioactivité induite dans ce détecteur est bien connue. On utilise habituellement à cette fin des plaques d'indium, d'argent, de rhodium ou des compteurs à indium.

Cette méthode est intéressante dans les nombreux cas où il est impossible d'utiliser des compteurs ordinaires à neutrons (au bore 10, par exemple), pour des raisons de vieillissement et de géométrie (ces appareils ayant, en général, des dimensions assez grandes).

Cependant, les sources de neutrons généralement utilisées émettent, en plus des neutrons, des rayons gamma en grande quantité, si bien qu'il est impossible de mesurer, dans le voisinage de ces sources,

l'activité induite dans les pastilles activées. Ceci nous a amené à adapter la méthode d'activation à nos besoins, en utilisant non plus des plaques, mais une solution activable circulant dans une tuyauterie souple qui l'amène, après activation, à l'endroit de la mesure, en dehors des rayonnements parasites.*

REALISATION D'UN APPAREIL

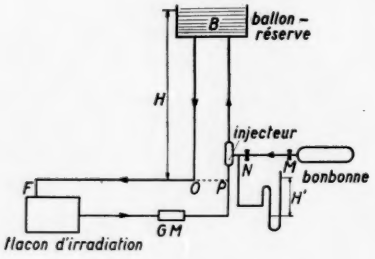

FIG. 1

Nous avons construit un premier appareil en verre suivant le schéma de la Fig. 1.

Par la tuyauterie *MN*, on injecte des bulles d'air comprimé dans le tube vertical *PB*. Il en résulte une différence de pression entre les points *P* et *O*, qui force le liquide à circuler dans le sens *OFPBO*.

L'irradiation de la solution a lieu dans le flacon *F*, placé au voisinage de la source de neutrons, et son activité est comptée à l'aide du compteur de Geiger–Müller *GM*.

La forme et la disposition de l'injecteur ont une grande influence sur la stabilité du fonctionnment de l'appareil. Après avoir utilisé les trois types d'injecteurs schématisés à la Fig. 2, nous avons adopté le type *C*.

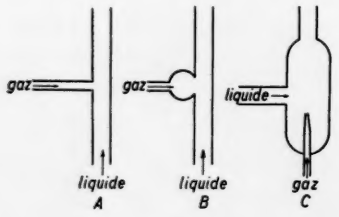

FIG. 2

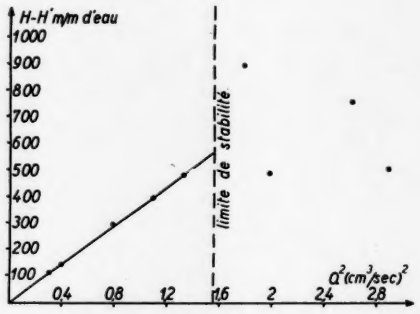

FIG. 3

Cet appareil expérimental nous a donné de très bons résultats et nous a conduit à réaliser l'appareil définitif équipé d'une pompe (schématisé à la Fig. 4) car le débit de solution *Q*, dans la zône de stabilité (Fig. 3) était trop faible.† Les conduites sont souples (tubes en polystyrène) et le flacon d'irradiation est obtenu par enroulement de la tuyauterie sur elle-même à l'endroit de la mesure. Les parties utiles de la pompe sont en acier inoxydable. Le comptage se fait par compteur de Geiger (20th Century, type B 12) et dérivateur.

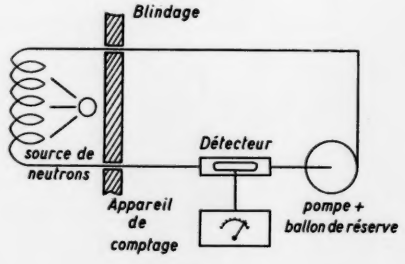

FIG. 4

* Initialement, nous avions envisagé de réaliser un ruban à base de matériau activable se déroulant à vitesse constante et traversant le flux à mesurer, mais ce système est difficile à construire et est inamovible, aussi l'avons-nous abandonné.

† Nous avons également essayé la mise en circulation de la solution par thermosiphon, mais nous avons dû l'abandonner à cause de l'instabilité du débit.

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ETUDE DU FONCTIONNEMENT DE L'APPAREIL

Désignons par:

T: la période de circulation de la solution dans le circuit,

t_s: la durée d'irradiation (durée moyenne de séjour du liquide dans le flacon d'irradiation),

t_c: l'instant du comptage, à partir du début de l'irradiation,

τ: la vie moyenne de l'isotope radioactif formé,

ρ: le rendement de l'installation de comptage,

I: la radioactivité induite dans le liquide du flacon d'irradiation,

$A = V\Sigma\Phi\tau$: la valeur de la radioactivité à saturation qui serait induite dans le liquide du flacon d'irradiation, la solution étant au repos (V désigne le volume du flacon d'irradiation, Σ la section efficace macroscopique de la solution, Φ le flux de neutrons).

a: le taux de comptage.

Nous supposons, dans cette étude simplifiée, qu'il n'y a aucun mélange ni aucune diffusion de solution radioactive dans la solution vierge.

1°—Si la tuyauterie est de longueur suffisante pour que l'activité résiduelle* puisse être négligée, on a:

$$I = A\{1 - \exp(-t_s/\tau)\} \tag{1}$$

$$a = \rho A\{1 - \exp(-t_s/\tau)\} \exp\{-(t_c - t_s)/\tau\}$$

Le taux de comptage a est l'image du flux moyen de neutrons Φ dans le flacon d'irradiation, puisque, toutes autres conditions égales d'ailleurs, ρ, t_s, τ, t_c, V, Σ, sont constants et par suite

$$a = k_1 \cdot A = k_2 \cdot \Phi$$

2°—Si l'activité résiduelle ne peut être négligée, lors du premier passage de la solution active au compteur, le taux de comptage vaut:

$$a_1 = \rho A\{1 - \exp(-t_s/\tau)\} \exp\{-(t_c - t_s)/\tau\};$$

au 2e passage au compteur, on a:

$$a_2 = a_1 + a_1 \exp(-T/\tau) = a_1\{1 + \exp(-T/\tau)\};$$

et au n^e passage au compteur:

$$a = a_1\{1 + \exp(-T/\tau) + \exp(-2T/\tau) \ldots + \exp(-(n-1)T/\tau)\}$$

En régime, c'est-à-dire pour $n = \infty$ (saturation), le taux de comptage a pour valeur:

$$a_s = \frac{a_1}{1 - \exp(-T/\tau)}$$

ou finalement:

$$a_s = \rho A \frac{\{1 - \exp(-t_s/\tau)\} \exp\{-(t_c - t_s)/\tau\}}{1 - \exp(-T/\tau)} \tag{2}$$

Dans ce cas, a_s, n'est l'image du flux de neutrons que si celui-ci varie lentement.

DISCUSSION

Il est évident que l'on a intérêt pour des raisons de précision des mesures, à réaliser un taux de comptage aussi grand que possible. Pour cela, il faut (voir formules (1) et (2)):

1°—réduire au maximum t_c et augmenter au maximum t_s, ce qui peut se faire lors de la construction de l'appareil en choisissant judicieusement les longueurs des canalisations;

2°—réaliser un rendement de comptage ρ maximum en utilisant toute la partie utile du compteur Geiger–Müller et une gaîne de compteur adéquate;

3°—augmenter A au maximum. Pour un fonctionnement déterminé et un type de solution donnée, A est fonction du volume et de la forme du flacon d'irradiation et de la teneur de la solution en matière activable. La teneur maximum en matière activable dépend de la nature du sel utilisé.

4°—choisir le radioisotope d'après les

* Due aux passages précedénts de la solution dans le flux de neutrons.

considérations que nous émettons dans la suite de ce paragraphe.

Pour suivre les variations du flux de neutrons Φ, on a avantage à se placer dans le cas où l'activité résiduelle est négligeable c'est-à-dire réaliser un circuit dont la période T est grande vis-à-vis de la vie moyenne τ du radioisotope utilisé.

Influence des phénomènes de diffusion et des mélanges

Si nous irradions la solution statiquement (sans circulation) et si nous mettons ensuite la pompe en marche après avoir retiré la bobine d'irradiation du flux de neutrons, la loi théorique du taux de comptage en fonction du temps est celle de la Fig. 5. Pratiquement, avec le montage initial et une solution aqueuse de nitrate d'indium, nous avons obtenu les résultats indiqués à la Fig. 6 (la constante de temps du dérivateur valait 20 sec).

De la comparaison des Figs. 5 et 6, nous déduisons que les phénomènes de diffusion et les mélanges des solutions vierge et activée sont très importants (diffusion statique dans tout le circuit; mélange de solution vierge et de solution radioactive par répartition parabolique de la vitesse dans les tuyauteries et par tourbillons dans la gaîne du compteur *GM*, la pompe, etc.).

Suite à ces phénomènes, une fraction des particules actives contenues dans un volume déterminé sont remplacées par des particules vierges. Il en résulte que la décroissance de l'activité spécifique de la solution (par unité de volume) est plus rapide que la décroissance radioactive naturelle et que les particules

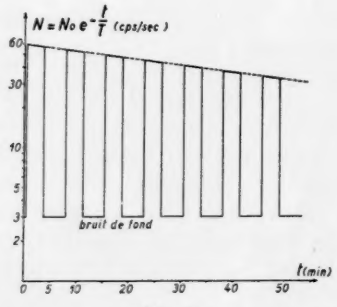

FIG. 5

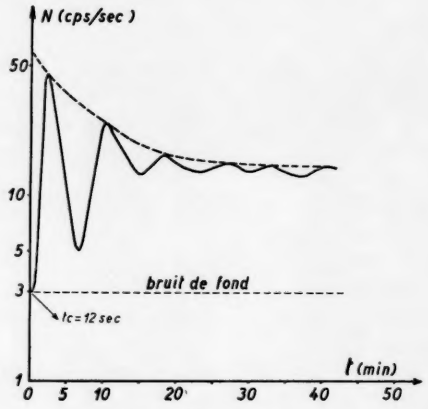

FIG. 6

actives n'atteignent pas toutes le compteur après le même temps $(t_c - t_s)$.

Choix du matériau activable

Nous considérons les cas où l'on désire suivre les fluctuations rapides du flux de neutrons.

Pour que la mesure de l'activité induite puisse se faire à une distance suffisante de la source de neutrons, en dehors des rayonnements parasites, le retard de comptage doit être de l'ordre de 1 à 2 min (le retard de comptage est le temps qui s'écoule entre la fin de l'irradiation et le début du comptage), et pour que l'activité induite dans le flacon d'irradiation ne décroisse pas trop entre la fin d'irradiation et le début du comptage, il faudrait choisir des radioisotopes à vie longue. Mais il est de plus nécessaire que l'activité résiduelle soit aussi faible que possible, ce qui exige un radioisotope à vie courte et une période du circuit, T, aussi grande que possible. Ces considérations conduisent au compromis qui consiste à choisir des isotopes dont la demi-vie est de l'ordre de quelques minutes. C'est le cas du rhodium Rh^{104} et de l'argent Ag^{108}.

Pour notre appareil, nous avons choisi une solution aqueuse de nitrate d'argent.

La composition isotopique naturelle de l'argent est la suivante

Ag^{107}: 51%

Ag^{109}: 49%

TABLEAU 1

Sel	Teneur en Ag de la solution saturée à 15°C	Autres constituants	Réaction d'activation parasite	Demi-vie du radioisotope	Section efficace microscopique de la réaction parasite
AgF	1210 g/l.	F^{19}	$F^{19}(th n,\gamma)\ F^{20}$ $F^{19}(1\ MeV n,\gamma)\ O^{19}$ $F^{19}(1\ MeV n,\gamma)\ N^{16}$	12 sec 29,4 sec 7,3 sec	9 mbarns 0,5 mbarn 4,5 mbarns
$AgClO_4$	1120 g/l.	Cl^{35} Cl^{37} O^{16}	$Cl^{35}(th n,p)S^{35}$ $Cl^{35}(th n,\gamma)Cl^{36}$ $Cl^{37}(th n,\gamma)Cl^{38}$ $O^{16}(1\ MeV n,p)N^{16}$	87 jours $4 . 10^5$ jrs 38,5 min 7,3 sec	0,34 barn 44 barns 0,6 barn 0,014 mbarn
$AgNO_3$	829 g/l.	N^{14} O^{16}	$N^{14}(th n,p)\ C^{14}$ $O^{16}(1\ MeV n,p)N^{16}$	5,7 ans 7,3 sec	1,7 barns 0,014 mbarn

et les réactions qui nous intéressent sont:

Ag^{107} (thn,γ) Ag^{108} (2.3 min); section efficace: 30 barns (1)
Ag^{107} (1 MeV n,γ) Ag^{108} (2,3 min); section efficace: 0,13 barn
Ag^{109} (thn,γ) Ag^{110} (24,5 sec); section efficace: 82 barns (2)
Ag^{109} (thn,γ) Ag^{110} (270 jours) section efficace: 2 barns (3)
Ag^{109} (1 MeV n,γ) Ag^{110} (270 jours); section efficace: 0,23 barn

La réaction (1) est la plus intéressante.

La réaction (2), qui donne Ag^{110} qui a une demi-vie de 24,5 sec, augmentera la sensibilité de la mesure pour autant que le retard de comptage ne soit pas trop grand.

Quant à l'isotope Ag^{110} de 270 jours de demi-vie, il est d'activité négligeable vis-à-vis des isotopes Ag^{108} et Ag^{110} (24,5 sec), eu égard à sa très faible section efficace.

Il s'agit maintenant de déterminer le sel qui convient, en tenant compte des solubilités et des autres constituants qui pourraient éventuellement être activés et donner lieu à des radioisotopes parasites.

Le Tableau 1 permet de faire la discussion.

A partir de ces considérations, on peut retenir soit le nitrate d'argent, comme nous l'avons fait, soit le fluorure d'argent qui permet d'obtenir la plus forte teneur en argent.

Pour des flux importants surtout, l'activation éventuelle du fluor n'est pas un inconvénient, les isotopes auxquels il donne lieu ayant des demi-vies courtes.

Signalons que le rhodium, sous forme de chlorure, de nitrate ou de sulfate est aussi intéressant et l'isotope formé, le rhodium Rh^{104} a une demi-vie de 4,3 min, ce qui justifie également le choix de cet élément comme matériau activable.

Pour terminer ce paragraphe, nous ferons remarquer que l'activation de l'argent se fait presque exclusivement par les neutrons thermiques et, par suite, si l'on désire détecter tous les neutrons, il y a lieu de les ralentir dans de la paraffine, par exemple, avant qu'ils n'atteignent la bobine d'irradiation.

RESULTATS

Les caractéristiques de notre appareil sont:
Volume total de solution: 1 litre
Poids de $AgNO_3$: 500 g
Volume de la réserve: 0,75 litre
Débit: 0,180 l./min
Temps de circulation: 3,75 sec (déterminé expérimentalement)
Distance source-compteur: 12 mètres environ
Retard de comptage tenant compte de la constante de temps du dérivateur: 75 sec (déterminé expérimentalement par irradiation statique, Fig. 7).

Dans le cas présent, le volume de la

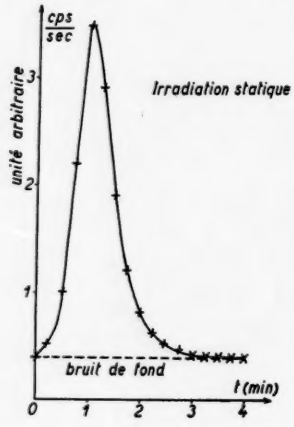

FIG. 7

réserve est tel que l'on a pratiquement à faire à un circuit infini et l'activité résiduelle peut être négligée (Fig. 7).

La Fig. 8 représente l'enregistrement des résultats obtenus lors d'une réaction Be(d,n) réalisée avec l'accélérateur du Centre de Mons et pour une émission totale maximum de $3 . 10^7$ neutrons/sec. La bobine d'irradiation était placée sous la cible. Les indications de l'appareil à nitrate d'argent suivent de très près celles d'un compteur au BF_3 utilisé comme témoin.

Ceci met en évidence les possibilités de détection offertes par cette méthode.

Remerciements—Nous exprimons nos vifs remercîments à Messieurs les Professeurs FRANEAU et WINKLER pour les directives qu'ils nous ont données et pour les remarques constructives qu'ils nous ont faites.

Nous remercions également Mr PERLAUX qui a construit la pompe que nous avons utilisée ainsi que MM. CHEVRY et DUPONT qui nous ont aidés lors des mesures.

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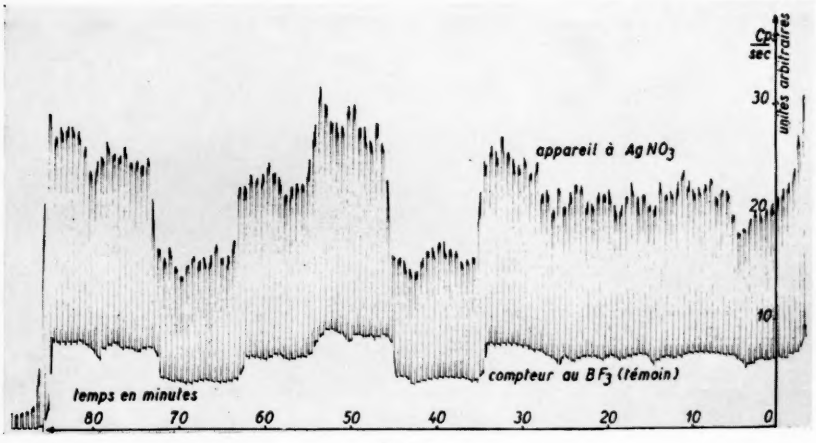
Cp/sec
30
20
10
unités arbitraires
appareil à $AgNO_3$
compteur au BF_3 (témoin)
temps en minutes
80
70
60
50
40
30
20
10
0

FIG. 8.

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The Specific Activity of Radium

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(*Received* 10 *November* 1958)

A critical assessment has been made of the published information on disintegration energies in the radium series, and a value obtained for the mean energy deposition per radium disintegration in sealed sources of known history. This, when combined with MANN's recent calorimetric measurements on the heating effects in several national primary radium standards prepared by HÖNIGSCHMID, gives a value for the specific activity of radium of $3{\cdot}655 \times 10^{10}$ disintegrations per second per gram, corresponding to a disintegration constant of $4{\cdot}326 \times 10^{-4}$/year, or a half-life of 1602 years.

L'ACTIVITÉ SPÉCIFIQUE DU RADIUM

Une cotisation décisive a été faite des renseignements publiés sur les énergies de désintégration dans la série du radium, et on a obtenu une valeur pour la moyenne de la déposition d'énergie par désintégration de radium dans le sources bouchées hermétiquement et ayant une histoire connue. Ceci a été réuni aux mesures calorimétriques récemment faites par Mann sur l'effet échauffant en plusieurs étalons nationaux primaires de radium préparés par Hönigschmid, donnant une valeur pour l'activité spécifique du radium de $3{,}655 \times 10^{10}$ désintégrations par seconde par gramme, ce qui correspond à une constants de désintégration de $4{,}326 \times 10^{-4}$ par an, ou bein une période de demi-valeur de 1602 ans.

УДЕЛЬНАЯ АКТИВНОСТЬ РАДИЯ

Сделан критический анализ опубликованных данных по энергиям распада в ряду радия и выведено среднее значение энергии, выделяемой при распаде препарата радия в запаянном источнике известного происхождения. Из этого, а также из проделанных недавно Манном калориметрических измерений тепловых эффектов для нескольких национальных первичных стандартов радия, изготовленных Хёнигшмидтом, выведено значение для удельной активности радия, равное $3{,}655 \cdot 10^{10}$ распадов/сек/гр, что соответствует константе распада в $4{,}326 \cdot 10^{-4}$ в год, или периоду полураспада в 1602 года.

DIE SPEZIFISCHE AKTIVITÄT VON RADIUM

Es wurde eine kritische Schätzung der publizierten Informationen über die Zerfallsenergie der Radiumreihe durchgeführt, wobei ein Wert für die mittlere Energieabgabe pro Radiumzerfall für eingeschmolzene Quellen bekannter Vorgeschichte erhalten wurde. Daraus ergab sich zusammen mit den vor kurzem von Mann vorgenommenen kalorimetrischen Messungen von den von Hönigschmid hergestellten Primärstandards mehrerer Nationen, ein Wert für die spezifische Aktivität von Radium von $3{,}655 \cdot 10^{10}$ Zerfällen pro Gramm, entsprechend einer Zerfallskonstante von $4{,}326 \cdot 10^{-4}$ pro Jahr, bzw. einer Halbwertszeit von 1602 Jahren.

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INTRODUCTION

ALTHOUGH the current definition of the curie severs its dependence on the specific activity of radium, there is still considerable interest in a precise knowledge of the disintegration constant of this substance. The most recent direct determinations of the specific activity of this nuclide, by KOHMAN *et al.*[1] and by SEBAOUN,[2] gave values (3·61 and 3·62 $\times$ 10^{10} disintegrations/sec/g respectively) significantly lower than the generally accepted value. The work had obviously been carried out with great care, using modern counting techniques, and threw considerable doubt on the earlier results which were grouped rather closely around a value of 3·67 $\times$ 10^{10}.

Recently, MANN[3] has made a very precise calorimetric determination of the rate of energy deposition from radium and its daughter substances, using three of the national primary radium standards prepared by HÖNIGSCHMID.[4] The rate of energy deposition was measured in a micro-calorimeter developed from the original design of CALLENDAR,[5] and the procedure was such that the errors usual in micro-calorimetry were self-balancing; the necessary calibration was effected directly against the Joule heating of a small resistance coil. MANN's value for the rate of energy deposition per gram of radium should yield, when combined with a value for the mean energy deposited per disintegration, an accurate independent value for the specific activity.

MEAN ENERGY DEPOSITED PER DISINTEGRATION

The disintegration scheme of the radium series is rather complex, but two factors make it possible nevertheless to assess the mean energy deposited per radium disintegration with relatively high precision:

(a) nearly 90 per cent of the total energy deposition results from α-particle emissions for which the energy release is very accurately known from magnetic deflection experiments;

(b) the alternative modes of decay (of Ra*A* and Ra*C*) are relatively so infrequent, and the energy then released so nearly the same as that from the principal mode of disintegration, that a quite insignificant error is introduced by ignoring these alternatives.

Energies of α-particle transitions

We have taken appropriately weighted average values from the compilation of BRIGGS;[6] the average total disintegration energies (rounded to the nearest keV) are:

Ra	4·855 $\pm$ 0·005 MeV
Rn	5·587 $\pm$ 0·001 MeV
Ra*A*	6·110 $\pm$ 0·001 MeV
Ra*C'*	7·827 $\pm$ 0·001 MeV
Po	5·406 $\pm$ 0·003 MeV

Energies of β- and γ-transitions

We have attempted to assess separately the energies associated with the penetrating radiation (which will be only partially absorbed in the calorimeter cups) and with the radiation completely degraded within the calorimeter (β-particles, conversion electrons and, to a good approximation, X-rays).

Where available, mean β-particle energies deduced by the integration of β-spectra have been used; in some cases, however, it has been necessary to use the empirical relationship[7]

$$\bar{E}_\beta = 0{\cdot}3E_{\max}$$

with appropriate weighting in the case of complex spectra. We arrive at the following results:

Radium. The 187 keV γ-ray occurring in 5·9 per cent of the disintegrations is substantially internally converted. Taking the ϵ^-/γ ratio as 0·88[8] we find a mean contribution of 0·005 MeV per disintegration as conversion electrons, and 0·006 MeV per disintegration as γ-radiation. The recently noted branching going to the 488 keV level in radon[9] occurs to an extent negligible for the present purpose.

Radium B. We have assumed, as a

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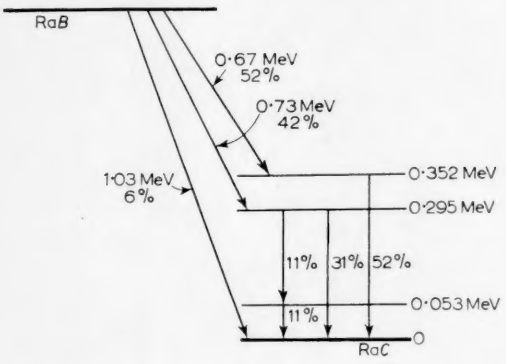
working hypothesis, the following disintegration scheme:[10–14]



From this we deduce a mean β-energy (using the empirical relationship) of 0·215 MeV per disintegration. Using the conversion coefficients obtained by ELLIS,[15] which are, in all essentials, confirmed by the more recent work of MLADJENOVIC and SLÄTIS,[16] we conclude that the mean energy per disintegration emitted as γ-rays is 252 keV and the mean contribution from conversion electrons 54 keV.

Radium C. A recent magnetic analysis of the Ra*C* β-spectrum[17] gives, on integration, $\bar{E} = 0{\cdot}66$ MeV per disintegration. The data of ELLIS on conversion electron yields lead to a value of 12 keV for this contribution. Using FEATHER's analysis of the γ-ray spectrum,[18] and allowing for the energy of conversion electrons, we find a mean γ-ray energy per disintegration of 1·535 MeV.

For the Ra$(B + C)$ complex we thus assume a total of 0·941 MeV per disintegration of energy carried by β-particles, conversion electrons and X-rays. This compares reasonably well with the value obtained by GURNEY[19] of 0·97 MeV.

Radium D. The total disintegration energy is only 65 keV, with 85 per cent of the transitions going to the 47 keV level in Ra*E*.[20,21] De-excitation of this level appears to proceed almost entirely by emission of conversion electrons and X-rays, involving $0{\cdot}85 \times 47$ keV per Ra*D* disintegration. The mean β-energy we estimate (by means of the empirical relationship) as 0·008 MeV.

Radium E. Several quite concordant calorimetric estimates of $\bar{E}_\beta$ exist.[22,23,24] We have taken $0{\cdot}33 \pm 0{\cdot}01$ MeV as an average value.

We thus find the following total rates of energy deposition per radium disintegration under conditions of secular equilibrium:

TABLE 1

	Energy completely absorbed (MeV)		γ-ray energy only partly absorbed in calorimeter (MeV)
	α	β, ϵ^-, X-ray	
Radium + short-lived active deposit	24·379	0·946	1·793
Ra*D* + Ra*E*	—	0·378	—
Polonium	5·406	—	—

CALCULATION OF DISINTEGRATION CONSTANT OF RADIUM

MANN's calorimetric measurements were made $19\frac{2}{3}$ years after the purification and sealing of the sources. Allowance must therefore be made for the incomplete growth of the Ra*D*–*E*–*F*– activity, and for the slight decay of the radium itself in the intervening period. Taking for this purpose the half-lives: Ra—1600 years;* Ra*D*—19·4

* For this relatively small correction factor the precise value assumed for the radium half-life is not critical.

years;[25] and Po—138·40 days,[26] we find by the normal procedure that the disintegration rates, expressed as fractions of the initial radium disintegration rate, will have been:

Ra, Rn, Ra*A*, Ra*B*, Ra*C*, Ra*C'*: 0·9915
Ra*D*, Ra*E*: 0·5024
Po (Ra*F*): 0·4926.

The three sources used by MANN contained in all 74·28 mg radium element when sealed by HÖNIGSCHMID in June 1934, and gave a total rate of energy deposition (in calorimeter cups of thickness equivalent to 0·184 cm lead) of 12223·9 μW in February 1954. Correction to this figure to allow for the incomplete absorption of the γ-radiation has been made using the absorption curve obtained calorimetrically by ZLOTOWSKI.[27] The rate of energy deposition for an "infinite" thickness of absorber is thus deduced as 12·944 mW, equivalent to $1{\cdot}0877 \times 10^{12}$ MeV/sec/g.

If Q is the specific activity of radium, U the specific rate of energy deposition, f_i the fraction of the initial radium disintegration rate attained by the ith member of the decay chain, and $\bar{E}_i$ the mean energy deposited per disintegration by this member, then

$$U = Q\,\Sigma f_i \bar{E}_i.$$

From this we deduce

$$Q = 3{\cdot}657 \times 10^{10} \text{ disintegrations/sec/g radium element.}$$

An alternative approach to the problem of correcting for incomplete absorption of the γ-radiation is to use ZLOTOWSKI's curve to estimate the fraction of the total γ-energy (1·793 MeV per disintegration) retained in the gold cups (stopping power equivalent to 0·184 cm thickness of lead) of MANN's calorimeter. From the curve this fraction is read as 0·103, and comparing now the energy deposition per second with that per disintegration on this new assumption, we find $Q = 3{\cdot}652 \times 10^{10}$ disintegrations/sec/g radium element. The substantial agreement between the two estimates of Q suggests that the basis of the calculation is fundamentally sound.

It is difficult to make an accurate assessment of the precision of this result. MANN quotes an error of $\pm 0{\cdot}5\%$ for the energy deposition per gram, although the internal consistency of his results is considerably better than this. A large fraction of the disintegration energy is carried by α-particles whose energy is accurately known, and we think it unlikely that our overall estimate of the energy per disintegration is in error by more than 0·1 MeV. Allowing for these two sources of error, we feel justified in quoting a final result

$$Q = 3{\cdot}655 \pm 0{\cdot}02 \times 10^{10} \text{ disintegrations/sec/g Ra,}$$

corresponding to a disintegration constant of $4{\cdot}326 \times 10^{-4}$ year^{-1}, and a half-life of 1602 years.

This result lies between the older values and those obtained by SEBAOUN and by KOHMAN *et al.*, lying rather closer to the former. If a more precise value for the radium disintegration constant were required, the procedure outlined above would appear to be capable of refinement to the extent needed to produce a definitive value for this quantity.

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technical notes

A Method by which Radioactive Material may be Transferred from a Paper Chromatogram to a Planchette*

(*Received* 23 *October* 1958)

In work with isotopes it is often convenient to carry out the isolation of labelled substances by means of paper chromatography. For accurate determinations the active material must be eluted from the paper and transferred to a planchette particularly when the radiation from the isotope is of low energy, in which case a direct determination of the activity on the paper will provide a rather crude estimation.

In this case the elution of the sample from the paper and its application to the planchette have previously been carried out in two separate steps. In order to save time and minimize the risk of accidental losses, an arrangement for automatic elution and application to the planchette in one step has been introduced.

Fogelström-Fineman *et al.*[1] have described a technique by which it is possible to transfer a whole paper chromatogram to a metal sheet. However when the problem is simply to elute and transfer individual spots, the procedure is too complicated.

A diagram of the arrangement used is shown in Fig. 1.

The elution fluid is poured into the glass tube *A*. A piece of asbestos filter *B* (sterile filter ST1/EKS) is placed into the lower part and adjusted to shape and density to give an even flow of elution fluid (1 ml in about 1 hr).

The tip of the glass tube touches the inner surface of the small glass funnel *C*, so that the elution fluid will flow evenly down this inner surface.

The glass funnel is fixed so that the tip can be placed at a suitable distance above the planchette. The internal diameter of the tip should be approx. 0·5 mm.

The section of the paper chromatogram which is to be eluted is put into the glass funnel after having been folded over the tip of a glass rod. The paper *D* is packed firmly into the funnel by means of the rod.

The elution fluid wets the lump of paper, fills the tip of the funnel completely and finally drips onto the planchette.

The planchette *E* is made of 0·6 mm thick aluminium and has concentric grooves of depth less than 0·01 mm (Ayres *et al.*[2]). The grooves are made by a rotating steel brush.

Before using the planchette it must be wiped with paper which has been wetted with a 1/10‰ solution of Dow Corning stopcock grease in chloroform. The very thin silicon layer ensures that the drops stay on the grooved area during the drying process.

The brass block *F* which is seen in cross section, is 280 mm long and is intended to accommodate ten planchettes so that ten applications can be carried out at once. The brass block is heated evenly by two aquarium elements *G*, each of 25 W. The heat is regulated with a variable resistance so that one drop will dry before the next one falls.

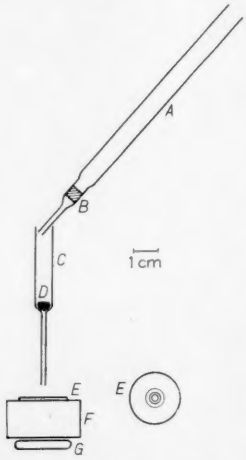

Fig. 1. Arrangement for transfer of a paper chromatogram to a planchette. *A* Glass tube. *B* Asbestos filter. C Glass funnel. *D* Section of a paper chromatogram *E* Planchette. *F* Brass block. *G* Aquarium element

Table 1 shows the results of elution and transfer of estradiol-3-*p*-iodobenzenesulfonate-I^{131} from paper to planchette.

For the elution chloroform-methanol 1 + 4 is used.

In each case 2 cm^2 of Whatman paper no. 1 containing approximately 2 μg of the substance with an activity of 51·90 counts/sec is used.

In some cases the fluid creeps a small distance up outside the tip of the glass funnel and leaves some radioactivity but this can easily be washed off with a few drops of the elution fluid.

* The work was supported by a grant from Statens almindelige Videnskabsfond.

TABLE 1. Elution and transfer of estradiol-3-*p*-iodobenzenesulfonate-I^{131} from paper to planchette

Experiment No.	Elution with 0·5 ml fluid	Elution with further 0·5 ml fluid	The tip of the glass funnel washed outside with a few drops of fluid	Total counts/ sec
1	49·70	0·09	0·31	50·10
2	47·30	0·05	1·90	49·25
3	47·30	0·31	1·84	49·45

The arrangement can also be used for elution with water. An example of this is seen in Table 2 where the results of elution and transfer of *p*-iodobenzenesulfonylglycine-S^{35} from paper to planchette may be seen.

In each experiment 2 cm^2 of Whatman paper no. 1 containing approximately 0·25 μg of the substance with an activity of 37·60 counts/sec is used.

The two examples show that the arrangement gives an effective elution. On average one finds 95 per cent and 97 per cent respectively of the original activity on the planchette.

The quality of the material to be eluted, the paper and the elution fluid are all factors deciding the result which will be obtained.

TABLE 2. Elution and transfer of *p*-iodobenzenesulfonylglycine-S^{35} from paper to planchette.

Experiment No.	Elution with 0·5 ml water	Elution with further 0·5 ml water	The tip of the glass funnel washed outside with a few drops of water	Total counts/ sec
4	35·90	0·83	0	36·73
5	34·10	2·67	0	36·77
6	35·70	0·75	0	36·45

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A Method for the Study of Fungicide Distribution by Farm Machinery Using Rb^{86}*

(*Received* 7 *July* 1958; *in revised form* 7 *October* 1958)

Introduction

THE application of fungicides to soil during seeding has become an important factor in protecting seedlings against diseases during their early growth.[1,2] This method of control, commonly referred to as row treatment, offers an opportunity for better protection than is possible by the application of fungicides to the seed surface before planting. Seed treatment may provide protection against soil fungi during the germination of the seed but in cases of severe infection, it cannot be expected to provide protection to young seedlings during the entire period of susceptibility.[3] In these cases, additional protection has been sought by spraying or dusting fungicides onto the overlaying soil. In California alone, more than 100,000 acres of cotton are treated annually in this manner. However, it is evident that the full potential of this type of protection has not been realized. Uniform distribution of the fungicide in the soil through which the seedling emerges is of primary importance. It may be optimal or completely ineffective depending upon the operating characteristics of the spray machinery. This note describes a method for using radioactive rubidium Rb^{86}, as a tracer to locate the fungicide after it has been applied to the soil under field conditions. This

* This investigation was supported by the United States Atomic Energy Commission and by the Agriculture Research Service, Crops Research Division, United States Department of Agriculture.

method provides for the first time the means for evaluating the effectiveness of various applicators.

Experimental

A tractor-drawn cotton seed planter was used for these experiments. It was equipped with a spray device which was designed to feed the fungicide solution to spray nozzles located before and after a wheel designed to press the seed into the soil. This machine is shown in Fig. 1.

2·8 mc of Rb^{86} in 0·1 N HCl were added to the supply tank of the planter which contained sufficient water to make a final isotope concentration of 0·75 μc Rb^{86}/ml. This liquid was applied at the rate of 500 ml per 100 ft row (3·75 μc/ft). The nozzle pressure was 30 ψ and the planter was drawn at 2·6 mile/hr.

The seed bed was cut in vertical cross section with a sharp spade and a small amount of soil was removed from one side of the cut. The face of each cut was sprayed with lacquer to prevent the soil from crumbling when profiles of approximately 4 mm thickness were removed. Radioautograms were obtained by superimposing no-screen X-ray film over the profile for 24 hr.

Results and discussion

The radioautogram in Fig. 2a shows how the Rb^{86} (and presumably the fungicide) was concentrated in a small band at the bottom of the seed bed when it was sprayed from a flat-fan nozzle located in front of the press-wheel. The liquid was sprayed directly on the seed in the open seed furrow. This type placement suggests good protection against preemergence seed decay but would offer little protection against postemergence damping off of the seedling. The radioautogram in Fig. 2b illustrates the distribution obtained when the liquid was sprayed from a hollow cone nozzle located behind the seed press-wheel. Here the liquid was directed onto the soil as it folded into the furrow over the seed. In contrast to front placement, nearly all the rubidium was deposited above the seed near the soil surface. In this case, the seedling—but not the seed—would be protected from infection.

Figs. 2c and 2d are radioautograms which represent the isotope distribution pattern obtained when the liquid was sprayed onto the seed furrow by front and rear nozzles simultaneously. Although the liquid was not uniformly distributed throughout the 2 in. × 2 in. seed bed, better protection would have been offered to both the seed and seedling.

Radioautographic visualization has thus proven to be a valuable aid in the evaluation of distribution patterns put out by liquid spray applicators. In addition, radioactive rubidium, Rb^{86}, proved to be an excellent isotope for this type research. Its half-life of 19·5 days was long enough to permit ample experimentation with seed beds, nozzle settings, and soil profiles; but short enough so that the field plots soon became available for other research projects. The isotope is inexpensive, relatively non-hazardous, and is available at high specific activity. Of even greater importance, however, was the ease with which the equipment was decontaminated. Unlike P^{32}, the isotope usually chosen for this type of research, Rb^{86} was completely removed by washing with cold water.

Acknowledgement—The authors gratefully acknowledge the technical assistance of Messrs. J. R. Tavernetti and J. Harvey.

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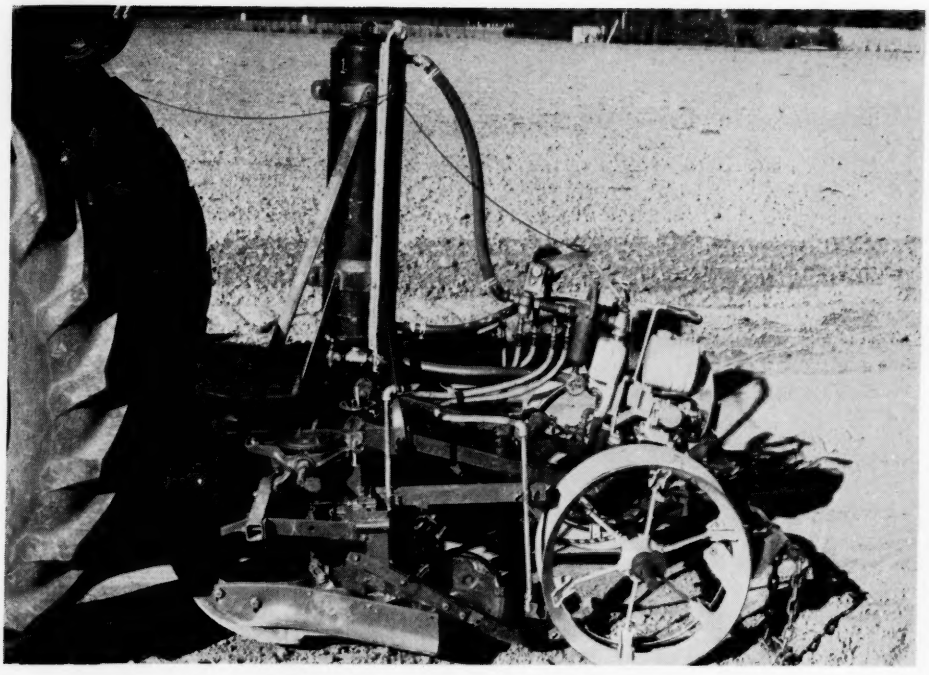

FIG. 1. Cotton seed planting machine equipped with spray nozzles located immediately before and after the seed press-wheel.

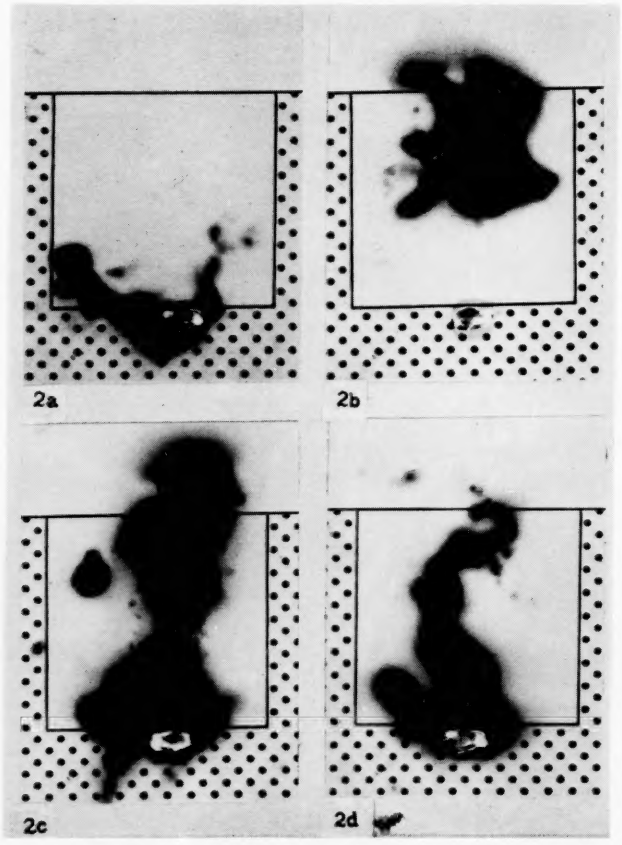

FIG. 2. Radioautograms of the soil vertical profiles taken after the Rb^{86} solution was applied by various nozzle placements. A grid is used to delineate the 2 in. × 2 in. planted furrow, and a cotton seed is shown at the bottom of each furrow.

2a, flat-fan spray nozzle located before the press-wheel; 2b, hollow-cone spray nozzle located after the press-wheel; 2c and 2d, both nozzles operating simultaneously.

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Abstracts of the Introductory Papers Presented at the International Atomic Energy Agency–World Health Organization Seminar on Medical Radioisotope Scanning Techniques and Results

Vienna, Austria, February 1959

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Theory of Isotope Scanning. G. L. BROWNELL, Physics Research Laboratory, Massachusetts General Hospital, Boston, Massachusetts.

The visualization of isotope distributions is an important aspect of the medical use of radioisotopes. The sensitivity patterns of various collimating systems are compared and their efficiency and resolution calculated. The collimating systems considered consist of cylindrical and tapered apertures, focusing collimators, and coincidence detection of annihilation radiation. A general theory is derived to give the optimum isotope concentration for each of the systems.

A similar theory is derived to cover the scintillation camera and a comparison is made of the optimum isotope concentration of this device in relation to scanning methods. A modification of the camera concept for use with annihilation radiation is discussed.

Various recording systems are compared as to efficiency and information presentation.

Problems of Collimation. HIROTAKE KAKEHI, Dept. of Radiology, Chiba University Hospital, Chiba, Japan.

Collimation is one of the most important problems in radioisotope scanning. It is closely related to the resolution of a scanning device. Any improvement in resolution is usually accompanied by a corresponding decrease in sensitivity, so that the design of a suitable collimator is the result of a compromise between resolution and sensitivity.

A number of different types of collimators have been designed for clinical use. They can be classified in the following way:

A. Single hole collimator
   - (i) Cylindrical
   - (ii) Conical, inverted
   - (iii) Conical, obverted

B. Slit collimator

C. Multichannel collimator
   - (i) Focused
     - (a) Honey cone
       - (1) Several to 280 holes
       - (2) Hexagonal or round shaped holes
     - (b) Spiral plug (Miller)
     - (c) Split plug (Miller)
   - (ii) Non-focused (Scott Cone)

In order to determine the most suitable type of collimator for a specific diagnostic problem, the response pattern of the detector must be known. This pattern can best be visualized by constructing an isoresponse curve which shows the absorption of the beam in a medium similar to human tissue.

However, even by determining the relative dosage at various points of the pathway of the beam in air, we are able to demonstrate the characteristics of a collimator.

Taking into account the various points mentioned above, the problems of choosing the most practical collimator for clinical scanning will be discussed.

Photoscanning. M. A. BENDER and M. BLAU, Department of Radioisotope Research, Roswell Park Memorial Institute, Buffalo, N.Y., U.S.A.

Isotope scanning permits the non-traumatic localization of several types of human tumors. To obtain satisfactory visualization, a scanner must be capable of resolving small differences in isotope content between target and non-target tissues and presenting this data in a readily interpretable form. In addition, it must have sufficient flexibility to be adaptable to the variety of activity levels and target : non-target ratios encountered clinically. Since for the most part isotope scanning is a diagnostic screening procedure, the overall counting efficiency must be high so that the administered radioactivity can be kept as low as possible.

A scanner meeting these needs has been constructed. The data presentation system, based upon the marked voltage dependence of the light output of a tungsten filament provides the high contrast necessary for visualizing small changes in count rate. It is possible to adjust the contrast and gain of the recording system to match the clinical requirements. A focusing collimator and large NaI crystal provide high efficiency, good resolution, and adequate depth response.

This instrument has been successfully used for the localization of human tumors of the brain, liver, and thyroid.

Basic Principles of Scintillation Counting. H. E. JOHNS and J. F. CEDERLUND,* Ontario Cancer Institute, Toronto, Canada.

The effect of the energy of radiation, the crystal size, the collimation of the beam and scattering on the pulse height distribution produced by monoenergetic radiation will be discussed. These aspects will be related to scintillation scanning. The effects of voltage on the operation of photomultipliers and so-called plateaus will be dealt with. Glow transfer tubes for counting will be dealt with and a useful subtraction circuit for comparing the counting rate from two separate scintillation counters will be presented.

The Scintillation Camera. H. O. ANGER and D. J. ROSENTHAL, Donner Laboratory, Berkeley 4, California, U.S.A.

A short description is given of earlier forms of the γ-ray camera. The principle of operation of the scintillation camera is reviewed. Here the locations of scintillations occurring in a flat thallium activated sodium iodide crystal are determined from the amount of light picked up by a number of phototubes simultaneously viewing the crystal. The signals from the phototubes are fed to a deflection computor circuit which reproduces the scintillations on a cathode ray tube screen. There they are photographed by a conventional scope camera. Examples are shown of the resolution now obtained as shown by test phantoms. A discussion is presented of the camera's use in visualizing the thyroid in clinical practice.

Detection of Liver Tumors with I^{131} Rose Bengal. M. A. BENDER and M. BLAU, Department of Radioisotope Research, Roswell Park Memorial Institute, Buffalo, N.Y., U.S.A.

It is possible to visualize tumors of the liver utilizing isotope scanning techniques. I^{131} labelled Rose Bengal administered intravenously localizes quite specifically in functional liver tissue. Space-occupying lesions in the liver do not concentrate this dye and they therefore appear in the scans as areas of decreased radioactivity.

Utilizing high contrast photoscanning techniques and focusing collimators we have been able to make a correct diagnosis in 90 per cent of the cases studied. Tumors 2 cm in diameter or larger anywhere in the liver are readily visualized.

* On leave of absence from Radiofysiska institutionen, University of Lund, Sweden.

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Liver Scanning with Colloidal Radiogold. L. Donato, M. F. Becchini, S. Panichi, Centro di Medicina Nucleare, University of Pisa, Italy.

The authors report their experience in the use of colloidal Au^{198} for liver scanning.

To obtain a good differentiation of liver from surrounding organs and tissues, a tracer dose of 2.5 μc/kg is usually required. The whole scanning procedure, starting 30 min after intravenous injection, takes about 90 min, when carried out with fully automatic equipment.

Upper and lateral liver contours are usually better defined than the lower one; the use of focusing collimators (honeycomb type) increases the resolution remarkably.

In normal conditions the liver is the only organ clearly evident on the scan; the spleen may also become evident in some cases of splenomegaly and liver cirrhosis, probably on account of the reduction of reticuloendothelial system of the liver.

In the experience of the authors, the efficiency of the technique is very poor for the detection of liver metastases of small size, not inducing changes of the volume and shape of the liver. In fact, uncertain results have been obtained even in cases of micronodular metastatic diffusion, confirmed at operation.

The Au^{198} scanning may be of help in cases with diffuse or zonal enlargement, whatever the origin, in order to establish whether the changes are due to enlargement of normally functioning tissue, or to the presence of intrahepatic pathologic entities. It has been found very helpful to combine liver scanning with X-ray examination of liver contours after carrying out pneumoperitoneum, in order to compare anatomical and functional patterns.

Scintigraphs and X-ray contours are normally superimposable, and the finding of significant discrepancies may be helpful in evaluating the possibility of surgical or radiation treatment in patients with tumours, especially of the gastrointestinal tract. Of course, a negative result will not rule out the possibility of liver metastases.

Original scintigraphs and corresponding X-ray films are presented, and the results of major interest are discussed.

Positron Scanning of Liver and Pancreas. S. Aronow, R. Thors and G. L. Brownell, Physics Research Laboratory, Massachusetts General Hospital, Boston, Massachusetts, U.S.A.

The success of the positron scanning technique in the localization of brain tumors has suggested its application to other organs. Zn^{62} is used in an attempt to delineate the pancreas and Cu^{64} in various forms is used to delineate the liver. The problem of visualizing the pancreas is particularly difficult because of its small size and the presence of large organs in the vicinity which concentrate zinc. Several approaches to this problem are discussed. Cu^{64} in simple ionic form and in the form of copper versenate concentrate to a marked degree in the liver. Positron scans of the liver would seem to offer considerable promise for successful diagnosis of various liver disorders. Data is presented on the distribution of several isotopes and compounds in animals.

The Distribution of a Pure Beta-emitter in the Human Body. Problems and Preliminary Results of Bremsstrahlung Measurements *in vivo*. H. G. Mehl, Strahleninstitut der Freien Universität, Berlin, Germany.

In vivo measurements of the distribution of a pure β-emitter in the human body were previously limited to the location of radioactivity in superficial tissues only, due to the short range of the β-particles in tissue. During the last few years the analysis has been extended by means of bremsstrahlung measurements to activities in deep-lying tissues.

The present paper deals with problems and results of this new technique. Based on an analysis of the physical nature of this radiation, the construction of suitable detection devices is discussed. The theoretical and experimental work done in this field are reviewed. In order to make a proper interpretation of the results obtained, it is

necessary to analyse the various factors involved. These include particularly the area "seen" by the detector, the specific activity of the tissue seen and the depth of the organ under consideration. A discussion of the results of such measurements already published will permit an assessment of the present situation and of the nature of the problems still unsolved.

Profile Counting. E. Eric Pochin, Medical Research Council, Department of Clinical Research, University College Hospital Medical School, London, England.

In "profile counting", a counter is moved progressively along the whole length of the body, and is so collimated that, at each position, it records the radioisotope content of the whole width of the body, but of only a short section of its length. If the counting rate at each position is plotted against the distance of the counter from the vertex of the head, the "profile" so obtained gives a rapid and quantitative measure of the radioisotope distribution throughout the body. When a suitable isotope is selectively concentrated in certain organs or tissues of the body, the profile will show peaks indicative of the sites and extent of such concentration, the organs concerned being identified by two dimensional mapping, and profile counts continued to follow the turnover or changes of concentration in these organs.

This technique has been used in the study of I^{131} concentration and metabolism in thyroid carcinomata, and its value in the management of the radioiodine treatment of such tumours will be discussed. It has also been used in examining the distribution of labelled thyroxine and tri-iodothyronine after intravenous administration, and of yttrium-90 oxide particles after intrapulmonary artery injection; and of other isotopes by gamma radiation or bremsstrahlung. The method gives a clinically convenient simplification of whole body mapping which lends itself particularly to the quantitative comparison of isotope distribution at different intervals after a radioisotope dose, or after successive doses.

Coincidence Scanning with Positron-emitting Arsenic or Copper in the Diagnosis of Focal Intracranial Disease. William H. Sweet, John Mealey, Gordon L. Brownell and Saul Aronow, Departments of Surgery and Medicine, Harvard Medical School and Neurosurgical Service and Physics Research Laboratory, Massachusetts General Hospital, Boston, U.S.A.

This is a report on coincidence counting in man of the paired annihilation gamma rays from positron-emitting copper or arsenic. We discuss the relevant biological behavior of inorganic arsenate and arsenite, of copper versenate, and the results of using these substances during automatic scanning to localize intracranial masses.

Radioassay of biopsies of the principal normal cephalic tissues, of various types of neoplasms, of hematomas, abscesses and zones of demyelination were carried out. With arsenic the ratios of concentrations of tumor to normal brain were up to 30 for meningiomas. The remaining main tumor types in order of decreasing concentrations of isotope were acoustic neuroma, glioblastoma, metastatic malignancy, and astrocytoma. The high tumor uptake with arsenic persists long enough so that repeat scans one day after injection are valuable. The muscle/brain ratio of concentrations of *circa* 3 is high enough to interfere with the accuracy of diagnosis in lesions beneath the lower temporal and expecially the upper nuchal masses of muscle. Hematomas, abscesses and zones of demyelination also have high enough ratios to permit localization in the majority of patients. The results on biopsies containing copper versenate showed similar ratios insofar as ascertainable from fewer samples. The meningiomas are a probable exception yielding lower ratios with the copper.

On the basis of radioassay both of urinary excretion and of the full range of tissues obtainable at autopsy we compute the total whole body radiation with As^{74} to be about 3.2 rads after the usual scanning dose of 2.3 mc/70 kg. The kidney receives about 12.7 and the liver 9.7 rads. The corresponding figures for Cu^{64} are 0.325 rads to the whole

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body, but with a dose to the liver of 3.2 rads because this organ takes up about half of the administered versenate.

The automatic scan includes in two simultaneously evolving side views a coincidence count or positrocephalogram (PCG) and a plot of the asymmetry of the total γ-radiation, an asymmetrogammagram (AGG). A sagittal PCG is also taken. The lateral scan requires 40 min, the sagital 20 min.

Of the more than 3000 scans carried out we report here only the 385 performed in the last $3\frac{1}{2}$ yr on a special group of 334 patients, who nearly all proved to have focal, usually space-taking lesions and on whom we have a gross anatomical and histological diagnosis established after surgery or autopsy. In this group a correct diagnosis was made in 80 per cent of 249 tumors scanned with arsenic and in 70 per cent of 84 tumors scanned with copper. In a previous series of 207 arsenic scans in a similar group we localized only 69 per cent of the tumors. In the current series only 3 of 83 glioblastomas, and 3 of 34 meningiomas were missed with arsenic. At least one tumor was localized with arsenic in 85 per cent of those with one or more malignant metastases. The results with copper were not quite as good in any of these 3 major categories. Of the 182 tumors of one or both cerebral hemispheres studied with arsenic the correct diagnosis was made in 165 or 91 per cent; with copper there was an 81 per cent success in 64 patients of this type. Since it is especially the small cerebral tumors which are likely to be missed, by angiography or pneumography at a time when they are surgically resectable, this is perhaps the most important contribution of the method to date. In contrast we did poorly with subtentorial tumors, missing 23 of 39 or 59 per cent.

In the non-neoplastic group we localized 7 of 8 subdural hematomas with arsenic, none of 3 with copper. Verified intracerebral clots were spotted in 4 of 5 cases with arsenic and in 1 of 3 with copper. All 10 abscesses were found with arsenic and 3 of 4 with copper. In all 3 patients with leukoencephalopathy the arsenic scans indicated the major areas of demyelination. Of 10 patients who had had a total of 16 scans and who were subjected to craniotomy with a resulting negative exploration, there were only two in whom a diagnosis of definite focal abnormality had been made on the scan—one with arsenic and one with copper.

Diagnosis of Intracranial Lesions by Gamma-encephalography, Using Human Serum Albumen Labelled with Iodine-131. THÉRÈSE PLANIOL, Institut National d'Hygiène, Paris, France.

Six hundred patients were examined by means of serum albumen labelled with I^{131}. Radioactivity was read twice with a scintillation counter in contact with the skull, 2 hr and 24 hr after the radioactive injection.

Of 175 intracranial tumours, 150 were accompanied by a focus of persistent gamma hyperactivity. Of those not detected by the examination, half were tumours of the hemispheres and half of the posterior fossa and pineal body. Abscesses, haematomata and cirsoid aneurisms were detected. In one-third of the cases acute cerebro-vascular lesions produced abnormal readings, half of which had the peculiar appearance pathognomonic of softening (or thrombosis); the others resembled tumour graphs, the only difference being that the abnormal readings associated with acute vascular lesions disappeared in a few weeks. Two-thirds of these acute lesions were associated with a negative gamma-encephalogram. Arterial aneurisms, non-tumorous epileptogenic foci, and various purely neurological conditions gave normal results in 96 per cent of cases.

Brain investigation by radio-albumen can provide valuable information not only on the presence and exact location of a neurosurgical injury but also on its nature. In particular, it seems very likely to detect a meningioma, glioblastoma or metastatic growth. These properties, together with information on positive diagnosis and location, make it a specially useful neurodiagnostic method.

Gamma-encephalography also seems likely to be one of the most reliable ways of detecting relapses and of following-up the effects of medical treatment or radiotherapy.

Scanning in Non-cancerous Thyroid Disease. RUDOLF HÖFER and HERBERT VETTER, Radioisotope Laboratory, Second Medical University Clinic, Vienna, Austria.

There are two main groups of application of scanning procedures in the diagnosis of non-cancerous thyroid disease. The first covers the determination of the size and shape of normal and enlarged glands and the localization of aberrant thyroid tissue such as lingual thyroids and intrathoracic goitres. Results of such studies are of particular assistance to the surgeon in planning his operative approach. The second group comprises studies of the radioiodine distribution within a nodular goitre. Particular attention is paid to those single or multiple nodules which concentrate radioiodine to a higher extent than the surrounding uninvolved tissue. A clear distinction is made between these "hot" nodules and the "toxic" nodules which, in addition, are associated with clinical symptoms of thyrotoxicosis. Repeated scintigraphic studies following administration of thyrotropic hormone and desiccated thyroid are of value in the differential diagnosis of such nodules.

Scanning in Thyroid Cancer. FRANZ K. BAUER, Radioisotope Centre, University of Southern California School of Medicine, Los Angeles, California.

Scanning in thyroid cancer is of value in:

1. The preoperative diagnosis of a thyroid nodule;

2. The localization of thyroid cancer metastases;

3. The treatment of thyroidectomized patients with metastases from thyroid cancer.

The appearance of thyroid nodules on the scintigram is described. Some preliminary results of the use of radiophosphorus and external counting with a Geiger–Mueller tube of "cold" nodules are reported.

Localization of thyroid cancer metastases with particular emphasis on the use of thyrotropic hormone is described. With this method three-fourths of all patients with metastatic thyroid cancer were found to have functioning metastases. The technique of ablation of normal thyroid remnants follow total thyroidectomy and the treatment of metastases is discussed in detail. Scanning of metastases is the best method to follow the patient's progress.

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Summary Report and Proceedings of the Food and Agriculture Organization (FAO) European Meeting on the Use of Ionizing Radiations for Food Preservation*

Harwell, England, November, 1958

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A. Summary Report of the Meeting

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* To be published in *Int. J. Appl. Rad. Isotopes*, Volume 6.

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book reviews

FRIEDRICH ELLINGER: **Medical Radiation Biology.** Charles C. Thomas, Illinois; Blackwell, Oxford, 1957. xxxiv + 945 pp., £7.0.0.

No other book in English covers the same ground as this. It is mostly devoted to a systematic survey of the local and general effects of ionizing radiation but sections are included on the biological and clinical effects of visible light, ultraviolet and infrared radiation. The emphasis throughout is on effects in man, though there are copious references to experimental work on animals. Indeed there is a total of 4600 references, each with its title. The book is written for the medically qualified reader: no special knowledge of physics is assumed. It may be described as a widely based, academic introduction to radiotherapy without any attempt to provide detailed advice on treatment.

The book is well produced but by British standards is very expensive. It is a large book and an appreciable part of its bulk is due to its verbose and repetitive style. Sometimes the wrong English word is used, though without producing error or ambiguity, and there are also a number of misprints. The academic approach leads to an exaggerated emphasis on classificatory terminology, e.g. true and pseudo-antagonism (p. 102), and the terms used are sometimes wrongly defined, e.g. the definition given of complete additivity (p. 102) is correct only if 100 per cent effect is in fact produced by double the dose which produces 50 per cent effect, which is rarely the case and which in any event is irrelevant to the real definition. There are other errors, sometimes important, e.g. that "time and intensity may be varied within a wide range namely between ratios of 1 : 4 and 1 : 900 before changes in the biologic effect of a stated radiation dose become noticeable" (p. 96). Thus in spite of the author's immense industry the book cannot be recommended without reservations. It is however a mine of useful information collected from a wide variety of sources and should prove valuable as a reference work. There is no index but a very detailed table of contents.

R. H. MOLE

N. G. GUSSEV: **Leitfaden für Radioaktivität und Strahlenschutz.** VEB Verlag Technik, Berlin, 1957.

DIE kleine Tabellensammlung gibt ausführliche Anleitungen zur Berechnung aller Daten, die man bei der Arbeit mit radioaktiven Substanzen oder für die Berechnung von Strahlenschutzanordnungen benötigt. Der Gebrauch dieses Buches kann allen Ingenieuren, Medizinern, aber auch Chemikern und Physikern, die auf dem Gebiet der Radioaktivität arbeiten angelegentlich empfohlen werden. Einzelne Angaben, bei denen etwa die Halbwertszeit in Sekunden, Minuten, Stunden, Tagen und Jahren angegeben ist und ähnliches kann ohne Schaden gekürzt werden. Auf Seite 21 sollte bei einer Neuauflage in Tafel 6 bei der Gruppenunterteilung in "Gasförmige und flüchtige Spaltprodukte. β-Strahler u.s.w." darauf hingewiesen werden, dass die gasförmigen und flüchtigen Spaltprodukte ebenfalls β-Strahler sind. Auf Seite 22/23 Tafel 7 fehlen die Verzweigung beim RaA, ThA, AcA, die Verzweigung beim RaE undd ie $4n + 1$ Reihe und könnten ohne Schwierigkeit ergänzt werden.

F. STRASSMANN

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Use of Radioactive Isotopes in Investigations of the Diffusion and Thermodynamic Characteristics of Solid Solutions

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New techniques for determining diffusion and thermodynamic characteristics of solutions are discussed. Absorption methods (the "thick layer" and the "thin layer" methods) permit determination of diffusion coefficients whereby measurements of radiation absorption are not necessary. The impression method is an express method. The technique for determination of thermodynamic characteristics is based on exchange rate measurements. A non-isothermic method for the determination of diffusion characteristics and new techniques for measurements of the heat of dilution by the solubility to temperature ratio have been set forth during the last years. All methods were tested in a series of diffusion and thermodynamic measurements.

EMPLOI DES ISOTOPES RADIOACTIFS DANS LES ENQUÊTES SUR LA DIFFUSION ET LES CARACTÉRISTIQUES THERMODYNAMIQUES DES SOLUTIONS SOLIDES

Sont discutées de nouvelles techniques pour mesurer la diffusion et les caractéristiques thermodynamiques des solutions. Les méthodes d'absorption (les méthodes de "couche épaisse" et de "couche mince") permettent la mesure des coefficients de diffusion sans le besoin de mesurer l'absorption de la radiation. La méthode d'impression est une méthode expresse. La technique pour déterminer les caractéristiques thermodynamiques se base sur les mesures du taux d'échange. Dans ces dernières années ont été démontrées une méthode non-isothermique pour déterminer les caractéristiques de diffusion et de nouvelles techniques pour mesurer la chaleur de dilution au moyen de la proportion de solubilité à température. L'épreuve de toutes les méthodes fut achevée en une série de mesures sur la diffusion et sur la thermodynamique.

ПРИМЕНЕНИЕ РАДИОАКТИВНЫХ ИНДИКАТОРОВ ДЛЯ ИЗМЕРЕНИЯ ДИФФУЗИОННЫХ И ТЕРМОДИНАМИЧЕСКИХ ХАРАКТЕРИСТИК ТВЕРДЫХ РАСТВОРОВ

В статье излагаются новые методики измерения диффузионных и термодинамических характеристик сплавов. Абсорбционные методики (метод ''тонкого'' слоя и метод ''толстого'' слоя) позволяют измерять коэффициент диффузии без использования сведений о поглощении излучения. Метод отпечатка является экспрессным. Разработка методов определения термодинамических характеристик основана на измерении скорости обмена. В последние годы разработаны—неизотермическая методика определения диффузионных характеристик и методика измерения теплот растворения по зависимости растворимости от температуры. Все методики проверены на ряде примеров измерения диффузионных и термодинамических характеристик.

1

THE present theory of solids and the solution of important practical problems connected with the production of semi-conductors and heat resistant materials require a great amount of information on diffusion and thermodynamic properties of alloys.

This is connected with many difficulties such as the slow development of processes in solids, the non-equilibrium in the real solids, the particularities of their structure, etc.

The high sensitivity of radioactive substances, the simple technique of determining their concentration, the possibility of localizing the emitter by radiation absorption and scattering, as well as by other characteristics of these substances open up new possibilities for a methodical solution of this problem.

This paper is concerned with the methods worked out by the author and his collaborators in the Moscow Institute of Steel.

Out of the diversity of methods for determining diffusion characteristics, best adapted for the use of radioisotopes are absorption methods such as sample sectioning, measurements of the removed layer thickness, etc., as they require no tedious manipulations. However, the classical absorption method for determining the diffusion coefficient does involve measurements of the β-radiation absorption coefficients. Along with these measurements being complex and requiring in fact preparation of thin layers, absorption cannot be adequately described by the Beer law, especially for the case of a complex β-spectrum. Besides, such a description of the interaction of radiation with substance would ignore scattering phenomena (reflection, focusing, etc.). Thus it becomes necessary to eliminate absorption characteristic measurements.

This problem would be solved by finding out diffusion characteristics not dependent upon the laws of radiation absorption and scattering, and by working out an acceptable method for calculating these characteristics from experimental evidence. The activation energy will be shown to be a value of this kind.

The main result of a diffusion experiment using absorption techniques would be the value I/I_0 as a function of time. I and I_0 are values for β-radiation emitted by a sample coated with an active substance layer at a moment t and prior to diffusion annealing. I/I_0 is dimensionless and will depend only upon the diffusion coefficient D, upon absorption characteristics and time. The diffusion characteristics being independent of time I/I_0 will be determined by the Dt factor, as this is the only possible way to exclude the time dimension.

Thus equal Dt values will correspond to similar I/I_0. This permits ready determination of the activation energy.

In fact by measuring I/I_0 as a function of time at two temperatures (T_1 and T_2) it is possible to obtain the relation $D_1t_1 = D_2t_2$ from the values corresponding to equal I/I_0. Hence

$$\frac{D_1}{D_2} = \frac{t_2}{t_1} = \exp\left[-E/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right].$$

Thus knowledge of absorption characteristics is not essential for the determination of activation energy.

This method was tested in experiments on self-diffusion of silver.[1] Its disadvantage is the necessity of plotting a curve for $I = f(t)$ by a great number of experimental points. Its accuracy can be increased by annealing two samples at first at the same temperature and then at different ones.

However, the diffusion coefficient cannot be determined by this method. It would require techniques not necessitating measurements of absorption characteristics. The dimension theory would again be useful here. Since characteristics of the absorption coefficient type with an inverse to length dimension are to be excluded, a value of the length dimension should be introduced. The cross-section of a thin layer sample can be chosen as such a value. This was the basis of the thin layer method worked out by the author and KRYUKOV[2].

The method involves measurements of the variations in radiation intensity on the two sides of a thin plate ($\sim$0·1 mm) depending upon the time of annealing. Prior to the annealing some active substance is to be

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deposited on one of the sides of the plate by electrolysis. The radiation intensity at this side of the plate (I_1) would obviously decrease and that at the opposite side (I_2) increase with time. Thus it is necessary to choose the relative I_1 and I_2 values so that differentiation of the absorption and diffusion characteristics be possible.

Solution of the problem for the case in question, i.e. for a layer much thinner than the plate cross-section, and for a considerable time of annealing, can be written as:

$$C = C_0 \frac{h}{l}\left[1 + 2\cos\frac{\pi x}{l}\exp -\left(\frac{\pi}{l}\right)^2 Dt\right] \quad (1)$$

where h is the thickness of the layer, and l that of the plate. Hence

$$I_1 = \int_0^l cf(x, l-x)dx$$

$$I_2 = \int_0^l cf(l-x, x)dx$$

The expression $f(x,\ l-x)$ takes into account the absorption and reflection of radiation by the deposited layer.

It follows from equations (1) and (2) that

$$\frac{I_1}{I_2} = \frac{1 + k\exp(-mt)}{1 - k\exp(-mt)}$$

where m is a function of diffusion characteristics $\left(m = \frac{\pi^2 D}{l^2}\right)$ and k of absorption characteristics

$$k = \frac{2\int_0^l \left(\cos\frac{\pi x}{l^2}\right) f(x,\ l-x)dx}{\int_0^l f(x,\ l-x)dx}$$

Thus the differentiation of absorption and diffusion characteristics can be considered as achieved

$$\ln\frac{I_1 - I_2}{I_1 + I_2} = \ln k - mt.$$

The diffusion coefficient can be then calculated from the plot drawn in co-ordinates $\ln\frac{I_1 - I_2}{I_1 + I_2} - t$. Fig. 1 shows the kinetic curve obtained by the thin layer method for the case of self-diffusion in silver. The

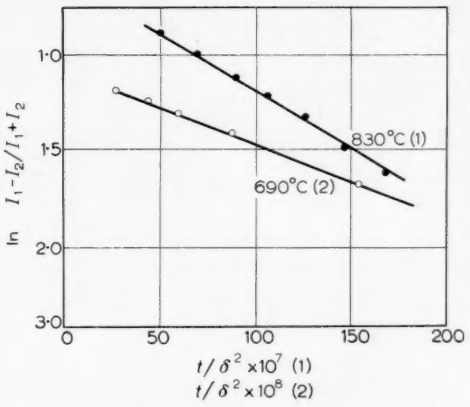

FIG. 1. Kinetic curves obtained by the thin layer method.

advantage of the method is its simplicity and also the fact that possible errors in the computation of I_1 and I_2 only slightly affect the expression $\frac{I_1 - I_2}{I_1 + I_2}$.

The method does not require prolonged annealing and has been used in a great number of experiments (as will be shown later). However, it necessitates preparation of thin layers, which is not always possible. Besides, doubts may arise as to the difference in the structure of the thin layer and of the bulk of the sample.

Thus the necessity arose for working out another method having no such drawbacks. This was done by the author and GEODAKYAN,[1] who have devised the "thick layer method".

Some other value related to the interaction between the radiation and the substance wherein diffusion takes place should be found for measurements, instead of the layer thickness value. This can be the radiation of a thick layer with uniformly distributed activity.

The method is based on measurement of the function $I = f(t)$ generally used in the conventional absorption technique

$$I = \frac{I_0}{\sqrt{(\pi Dt)}} \int_0^\infty f(x) \exp\left(-\frac{x^2}{4Dt}\right) dx$$

where $f(x)$ is the function already made use of.

By expanding $\exp -x^2/4Dt$ in series we obtain for high values of time

$$I = \frac{I_0}{\sqrt{(\pi Dt)}} \int_0^\infty f(x)\, dx.$$

Determination of the $\int_0^\infty f(x)\, dx$ value becomes necessary. This value can be obtained from calculations of the uniform activity sample radiation having a cross-section substantially exceeding $1/\mu$.

By denoting the β and γ radiation by $I_{\beta\infty}$ and $I_{\gamma\infty}$ and the initial radiations of the sample layer by $I_{\beta 0}$ and $I_{\gamma 0}$, and by introducing values

$$I_\infty = \frac{I_{\beta\infty}}{I_{\gamma\infty}}$$

and

$$I_0 = \frac{I_{\beta 0}}{I_{\gamma 0}}$$

it is possible to obtain the diffusion coefficient

$$D = \frac{I_\infty{}^2 \delta_\infty{}^2}{I_0{}^2 \pi m^2}$$

where m is the slope of the straight line representing the I/I_0 to $1/\sqrt{t}$ ratio. Fig. 2 shows the kinetic curve obtained by the thick layer method for self-diffusion of Ag.

Thus the thick layer method permits determination of the D value without measurements of absorption characteristics, sectioning of the sample and preparation of the thin layer.

The disadvantage of this method is its comparatively long time of annealing connected with the necessity to work in the asymptotic region corresponding to high T values.

The linear relation of I/I_0 and $I/\sqrt{t}$ can be taken as a criterion for the feasibility of using the asymptotic equation. The time when this relation sets in is connected with the energy of β-radiation and increases with it.

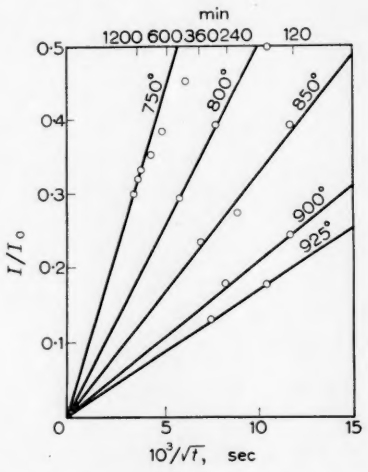

FIG. 2. Kinetic curves obtained by the thick layer method.

This time can be shortened by using filters eliminating the spectrum region corresponding to soft radiation.

The accuracy of this method is akin to that of the highest precision techniques. Another disadvantage of the thick layer method is the necessity for using samples with uniformly distributed activity. In the case of substances with high melting points such a sample can be prepared by wetting the powdered material with an active salt solution.

It would be difficult to devise an express method on the basis of the absorption technique, since the latter necessitates diffusion penetration comparable to the inverse value of the absorption coefficient. In working out the express method attention should be drawn first of all to the part of the sample where the change in concentration is most rapid. This requirement is met by

a surface coated with a thin layer of the active substance.

The surface concentration decreases with the time of annealing according to the relation

$$c = \frac{q}{\sqrt{(\pi Dt)}} \qquad (2)$$

where q is the amount of the deposited layer.

Thus instead of sectioning the samples it is possible to measure the surface concentration of active atoms. This can be done by different means. The author and GEODAKYAN[3] have chosen the impression method. An impression of the surface is obtained by means of microanode dissolution. The sample serves as the anode, the filter paper is impregnated with an electrolyte, for instance with NaCl, and pressed to the sample by the cathode.

After the current (~20 A) has passed for 3–5 min the paper is measured by a counter. The activity obtained (I) will be proportional to the surface concentration ($I = k_1 c$) of active atoms.

The q value is proportional to the γ-radiation intensity of the I_γ sample, i.e.

$$q = k_2 I\gamma$$

Equation (2) will be rewritten as

$$I = \frac{k_1 k_2 I_\gamma}{\sqrt{(\pi Dt)}}$$

The radiation of the sample ($I_{\gamma\infty}$) and that of the impression ($I_{\beta\infty}$) are measured in order to obtain the product of k_1 and k_2. Obviously

$$I_{\beta\infty} = k_1 C_\infty; \qquad I_{\gamma\infty} = \frac{C_\infty \delta_\infty}{k_2}$$

where δ_∞ is the sample thickness and C_∞ the radioisotope concentration in the sample.

An equation for the diffusion coefficient can be derived from these relations

$$D = \frac{I^2{}_{\beta\infty} \delta_\infty{}^2}{I^2{}_{\gamma\infty} \pi m^2}$$

where m is the slope of the straight line plotted in co-ordinates I/I_γ and $1/\sqrt{t}$.

The method was successfully tested in experiments on self-diffusion in Fe and Ag. Its accuracy corresponds to that of the sectioning method using high precision techniques. Fig. 3 shows the kinetic curve obtained by the impression method.

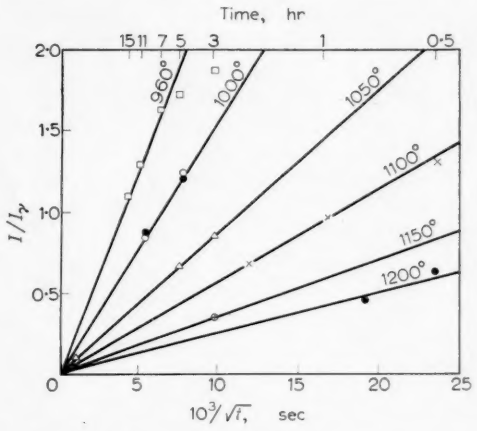

FIG. 3. Kinetic curves obtained by the impression method.

Besides considerably shortening the time of experiment (by a factor of thousands as compared to the sectioning method) the technique is extremely simple. Very small diffusion coefficients (~10^{-15}) can be determined by the impression method. It combines the two advantages of tracer techniques—the simplicity of concentration measurements and their high sensitivity.

It will be noted that the above considerations are valid for self-diffusion and solute diffusion in very diluted solutions usually met with in practice. For a general case corrections should be made for the proportionality of the impression radiation and the molar fraction of the solute.

Considerable difficulties may arise on using the impression method in the case of an alloy with a solute greatly differing in its position in the electrode potential series. This would require high current densities necessitated for the anode plating regime, and would greatly inconvenience standardization of the time of experiment.

A modification of the impression method

was worked out by GEODAKYAN.[3] Two electrolytic cells represented by the sample investigated and by a sample with uniformly distributed activity are mounted in series. Since a similar amount of electricity passes through both cells, measurements of neither time nor strength of the current are required and it is possible to use a high-voltage current.

Not only the solute, but also the solvent can be labelled. Then, instead of making an impression a small amount of the substance can be taken off the surface by any means available and its composition can be determined from isotopic activity. The labelled substances can differ in the nature of radiation, in its energy, in half-life periods, etc.

The techniques described were worked out for diffusion in a homogeneous medium, but there are not sufficient experimental and theoretical data on diffusion in heterogeneous systems. This problem is of great importance, first of all on account of the fact that real systems are heterogeneous.

Special attention will be paid to particularities of diffusion in a heterogeneous system, as they may lead to unusual values of diffusion characteristics and of the pre-exponential factor, being connected with the dependence of solubility on temperature, with phase transformations and with increased mobility due to local fusion. This in turn would give misleading values of the activation energy resulting in erroneous interpretation of the data obtained (as will be shown later). Further, the use of tracer technique, particularly of the absorption method, for simultaneous determination of diffusion characteristics and of the value for the state diagram of the solubility type, is of great practical interest. Various solutions of this problem will be discussed later. The difference in solute diffusion and self-diffusion is rarely taken into account in investigations on heterogeneous systems, whilst it has already been shown to be of great importance. This can be illustrated by heterogeneous systems involving equilibrium phases, for example saturated α- and β-phases in a simple system with limited solubility. Despite the concentration gradient there is no diffusion in such a system, as there are no gradients of the chemical potential or of the thermodynamic activity. This certainly does not mean that the diffusion coefficient is zero. Only the diffusion mobility energy is absent. However the rate of self-diffusion in a solution of this kind will be near to that of solute diffusion in a homogeneous system.

Besides being of methodical interest, the evidence obtained on diffusion in heterogeneous systems would be very valuable in establishing the reaction mechanism and in differentiating the kinetic and diffusion characteristics of new phase formation processes. First of all the study of concentration equalizing would yield data useful for the determination of the kinetic region wherein the process rate is governed by the rates of old phases destruction and new phases formation.

Evidence on the mechanism of processes accompanied by diffusion jumps would be of great importance. Thus it is necessary to find out whether the enhancement of vacancies in heterogeneous systems proceeds by some particular mechanism. A specific hydrodynamic flow resulting in the so-called Kirkendall effect, is known to occur on diffusion in a homogeneous system due to disparity of partial diffusion coefficients.

As will be shown later, hydrodynamic flows of the Kirkendall type will occur in heterogeneous systems even when partial diffusion coefficients are similar. The direction of this flow does not depend on the relationship of partial diffusion coefficients and always follows the disappearing phase. Formation of vacancies leading to destruction is also conceivable here.

There are two possible routes of carrying out experiments on diffusion. The first involves a very fine deposited solution layer differing in concentration from that of the homogeneous system, and in the second the layer is considerably thick.

In the first case the process will develop in the homogeneous region and its analysis will give only diffusion characteristics. In the second the first stage of the process may proceed in the heterogeneous region and then there may be an abrupt jump into the homogeneous region.

It will be noted that for separate investigations of the solute diffusion, apart from self-diffusion, the layer should differ from the sample in chemical, but not in isotopic composition.

Therefore the active constituent content of the sample should be similar to that of the layer, in other words the base should be active. Investigations on self-diffusion require a uniform chemical composition of the layer and an isotopic gradient. This is rather difficult to obtain, but since the solute diffusion is often more rapid than self-diffusion, the chemical composition of the deposited layer becomes identical to that of the base. Consequently self-diffusion sets in and is taking place for the main time of the experiment.

In the second case there will be a break in the kinetic curve representing the sample radiation as a function of time. This break corresponds to the saturated phase and is also observed when using the thin layer method.

According to WAGNER[4] the process accounting for the disappearance of the saturated layer is described by the equation

$$x = 2\gamma\sqrt{(Dt)}$$

where x is the thickness of the saturated layer and t is the time, γ being determined by

$$\frac{C_{I_0} - C_{I_{II}}}{C_{I_{II}} - C_0} = \sqrt{\pi}e^{\gamma}[1 - \operatorname{erf}\gamma]$$

C_{I_0} is the solute concentration in a homogeneous region, $C_{I_{II}}$ is the solute concentration in a saturated solution and C_0 is the concentration in a two-phase region.

The diffusion coefficient can be determined by analysis of the kinetic curve at times exceeding that which corresponds to the break in the curve.

The layer thickness being known the solubility can be calculated from the given equations. Such a method for the determination of solubility is feasible if the kinetic region, wherein the rate is dependent upon the phase transformations and not upon diffusion, is small as compared to the overall time of experiment. This is the main cause of the 5–7 per cent error in the given values for solubility of copper in silver and of iron in silver.

The kinetic region can be determined if the relation of radiation (I) to time is of a parabolic nature.

It may be shown that

$$\frac{I_0 - I}{I} = \frac{2}{\sqrt{\pi}}\sqrt{(\mu^2 Dt)}$$

where μ is the radiation absorption coefficient and I_0 is the initial activity. The deviation from the parabolic relation would show the existence of kinetic resistances.

The kinetic region is observed for a considerable time (hours) even in a system as simple as Ag–Cu, where one lattice is characteristic of the whole concentration range.

On using the thin layer method and at a thickness of the layer equal to $0{\cdot}01\mu$ there will be no breaks in the kinetic curves. If the deposited layers are $1–2\mu$ thick the kinetic curve will consist of 2 lines.

Figs. 4 and 5 show curves for the diffusion of silver into copper investigated by both methods. Fig. 4 corresponds to 750° and Fig. 5 to 800°C.*

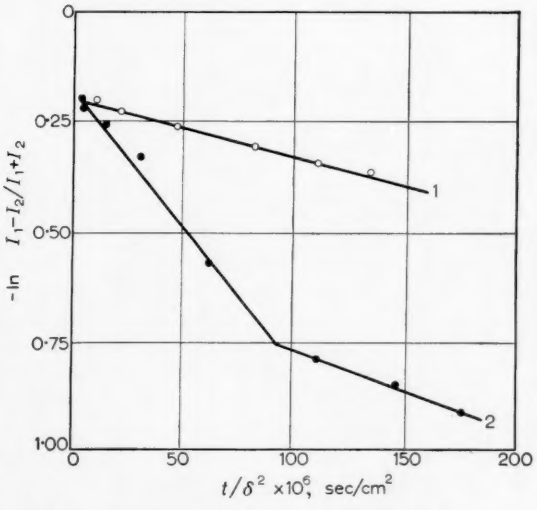

FIG. 4. Kinetic curve for diffusion of Ag into Cu, $t = 750$°C.

* The experiments were carried out by the author together with SOTZKOV.[5]

The eutectic temperature lies within these two temperatures. In the case of thick layers the slope of the line sections beyond the break can be seen to be similar to that of the lines obtained by the thin layer method. Thus in this part of the experiment the diffusion takes place in a homogeneous region.

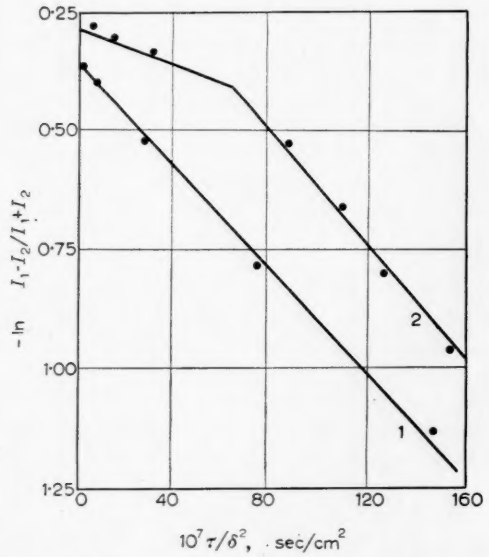

FIG. 5. Kinetic curve for diffusion of Ag into Cu, $t = 800°C$.

As can be seen from the slopes of the line sections preceding the break, at temperatures above and below the eutectic the diffusion is more and less rapid, respectively, than in a homogeneous medium.

Specific processes connected with melting and subsequent crystallization of the sample are observed above the eutectic temperature.

Let us take the simplest case. Let a thin silver layer be deposited over a thick copper layer and the annealing be made at a temperature above the eutectic. The initial (Ag and Cu) and the final (dilute β solution) states correspond to the solid phase, and the intermediate states to the liquid phase. A thin liquid layer will be immediately formed at the silver–copper interface. The next stage of the process would be the melting of both phases adjacent to this liquid layer. In a general case of any concentrations this layer can move along the sample.

The formation and disappearance of the liquid layer will considerably accelerate the diffusion processes.

At temperatures below the eutectic the diffusion processes in heterogeneous systems meet with considerable difficulties. This can be exemplified by diffusion at the interface of a saturated α-solution and copper. These phases are not in thermodynamic equilibrium and silver would diffuse from the α-solution into copper. However, detachment of silver atoms from the α-solution, even if made up by copper atoms, will lead to supersaturation of the phase with copper.

Thus the saturated α-phase is capable neither of giving away silver nor of capturing copper atoms. It would be susceptible to dilution by silver, but this is impossible under the conditions of contact with copper.

Diffusion would finally lead to the exchange of a fraction of the α-phase for the β-phase. In other words there would be a diffusion jump from a high value ($\sim$92 per cent) to a low one ($\sim$8 per cent). A process of this kind can occur either as a result of the α-lattice destruction, or of the β-lattice reconstruction.

Thus notwithstanding the constancy of the lattice the diffusion process will be topochemical. The transport of silver atoms into copper would lead to compression of the β-phase lattice and to expansion of that of the α-phase, i.e. to y hydrodynamic flow of the Kirkendall type.

The process of levelling out of the concentrations in the heterogeneous phase may proceed slowly even with a diffusion mechanism.

The proportionality coefficient for the interface displacement and $\sqrt{(Dt)}$ is a function of solubility and is likely to decrease with it.

The temperature coefficient of the overall diffusion process is connected with the temperature dependence of solubility, rather than with that of the true diffusion. If this is not taken into account, wrong, usually excessive, values for activation energies

would be obtained, particularly in comparing experimental results obtained above and below the eutectic temperature.

As can be seen from Table 1, slow development of the process below this temperature and the high process rate above it would result in values of the eutectic energy (E) many times higher than the true ones.

TABLE 1. The activation energy of diffusion in a system

Content (per cent)	$E\left(\frac{\text{g cal}}{\text{g mole}}\right)$
1	129,000
3	220,000

Special experiments were carried out by SOTZKOV[6] in order to verify the Kirkendall-type effect mentioned above. To reduce the amount of diluted gases the Ag–Cu alloys were vacuum melted. Molybdenum wires were wound round the samples made from these alloys and a silver or copper layer was deposited over these plates by electrolysis.

To be able to judge of the overall change in the sample volume a second row of molybdenum wires was wound round the samples at a distance of about 200 μ from the interphase.

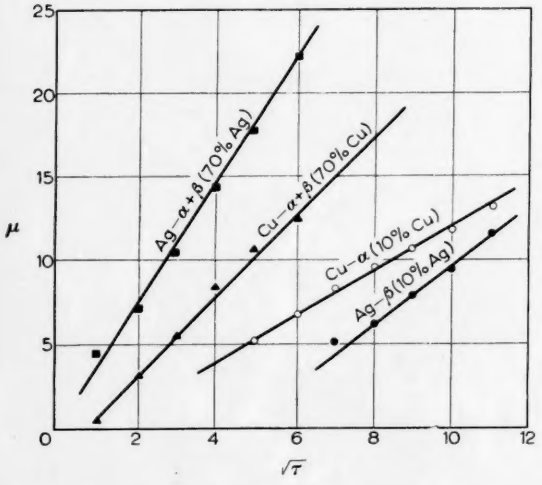

FIG. 6. Kirkendall effect in a heterogeneous system.

The temperature of annealing was 750°C and the distance between the wires was measured with an accuracy to within 0·5 μ.

Experiments were carried out at the interphase between silver and the β-phase and $(\alpha + \beta)$ (70 per cent of Ag), and between copper and the α-phase and $(\alpha + \beta)$ (70 per cent of Cu). It appeared that contrary to the Kirkendall effect the wires were always displaced in the direction of the two-phase regions. The displacement rate was dependent upon the composition of these regions. The results of these experiments are given in Fig. 6.

As had to be expected, at short times the displacement is not proportional to the time root. However, afterwards a region of diffusivity is observed for a long time during which this dependence is strictly fulfilled. The displacement of wires shows the occurrence of a hydrodynamic flow similar to that of Kirkendall.

All the methods examined require that the dependence of the diffusion coefficient on temperature and on the constants related to it (D_0 and E) be determined by isothermal measurements. Non-isothermal techniques permitting determination of the diffusion characteristics during one run, under conditions of a constantly rising temperature, were devised in collaboration with KRYUKOV and SOLDATOV.[7]

The diffusion coefficient in the equation for diffusion will depend upon time

$$\frac{\partial c}{\partial t} = D(t)\,\frac{\partial^2 C}{\partial x^2}.$$

The variable $y = \int_0^t D\,dt$ being introduced for simplification, the equation becomes

$$\frac{\partial c}{\partial y} = \frac{\partial^2 C}{\partial x^2}.$$

If there is a linear dependence of temperature on time

$$T = T_0 + \gamma t$$

$$D = D_0 e^{-\frac{E}{R(T_0 + \gamma t)}}.$$

If $\gamma t \ll T_0$, then $D = D^0 e^{\alpha t}$.

Here $D^0 = D_0 e^{-E/RT0}$ is the diffusion coefficient at the initial temperature and

$$\sigma = E\gamma/RT_0^2$$

$$y = \int_0^t D^0 e^{\sigma t}\, dt = \frac{D^0}{\sigma}(e^{\sigma t} - 1)$$

Introducing the variable $\tau = e^{\sigma t} - 1$ we get

$$\frac{\partial C}{\partial \tau} = \frac{D_0}{\sigma}\frac{\partial^2 C}{\partial x^2}$$

The equation obtained is the conventional isothermal diffusion equation. Hence any isothermal method and a corresponding diffusion equation can be used for investigating the non-isothermal diffusion, $e^{\sigma t} - 1$ being substituted for time and D^0/σ for the diffusion coefficient. Then D^0 and E, and the temperature dependence of the diffusion coefficient within the temperature range studied will be determined from experimental evidence.

A method similar to the thin layer method was chosen, the only difference being that it needed only measurements of I_1.

For a time sufficiently long and according to (1)

$$I = a - b \exp(-mt)$$

where $m = \frac{\pi^2}{l^2} \cdot D$

$$a = \frac{C_0 h}{l}\int_0^l f(l - x, x)\, dx$$

$$b = \frac{C_0 h}{l}\int_0^l f(l - x, x) \cos\frac{\pi x}{l}\, dx$$

It would be feasible to exclude constants a and b.

Thus one of the measurements (I_π) will be taken as a pole. Comparing the current point with the pole, we obtain

$$I_f = I_\pi = b \exp(-mt)\{\exp[-m(t - t_\pi)] - 1\}.$$

Or for two points

$$\frac{I_1 - I_\pi}{I_2 - I_\pi} = \frac{\exp[-m(t_1 - t_\pi)] - 1}{\exp[-m(t_2 - t_\pi)] - 1}$$

Substituting $e^{\sigma t} - 1$ for t and $\frac{D_0}{\sigma}$ for D and putting

$$n = \frac{\pi^2}{l^2}\frac{D^0}{\sigma}e^{\sigma t_\pi}$$

Simple transformations being made we obtain

$$Z_{1\cdot 2} = \frac{I_1 - I_\pi}{I_2 - I_\pi} = \frac{\exp[-n(e^{\sigma(t_1 - t_\pi)} - 1)] - 1}{\exp[-n(e^{\sigma(t_2 - t_\pi)} - 1)] - 1}.$$

The equation contains two unknown values σ and n. A graphic method was devised for their determination.

Taking $t_2 - t_\pi = t_1 = t_\pi$ we obtain

$$Z_{1\cdot 2} = f[\ln \sigma(t - t_\pi)].$$

A plot for this relation is drawn from experimental evidence. The plot is displaced along the X-axis until it coincides with the theoretical one involving curves for various n values.

n is found as the curve index, and σ is obtained from the degree of the scale shift.

The theoretical curves are given in Fig. 7.

The method was verified in measurements of silver self-diffusion. A special apparatus was constructed for continuous determination of β-radiation at temperatures increasing linearly with time.

The curve obtained for $I = f(t)$ was superimposed on the theoretical curves of the plot $Z_{1\cdot 2} - \ln(t - t_\pi)$. The values obtained for the activation energy and the pre-exponential factor were $E = 45{,}700$ and $D_0 = 0{\cdot}64$, i.e. were consistent with the evidence available.

The diffusion characteristics are closely

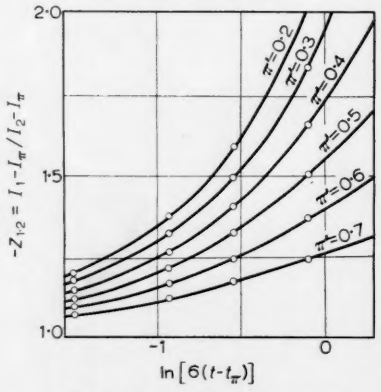

FIG. 7. Set of calculated curves.

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related to the thermodynamic ones. Out of the variety of possible applications of radioisotopes this method seems to be best adapted to the exchange techniques that were worked out by the author and, simultaneously and independently, by NESMEYANOV who was the first to publish the theory of the process.[8]

Three modifications of the exchange method were devised by the author.

The first, "the diffusion method," was worked out in collaboration with KRYUKOV, YANITZKAYA and GOLYTZYN.[9] It is based on the fact that the intersample diffusion resistance exceeds that inside the sample. In this it resembles the Knudsen method.

Two silica tubes placed one inside the other are fixed in an adapter. One of the samples is placed into the inner tube and the other between the inner and outer ones. This ensures resistance to capillary diffusion.

If a solute is diffusing towards a certain acceptor through the gas phase, then however complex be the diffusion process (volumetric, capillary, convective or surface) it will always be proportional to the solution concentration at the edge of the sample due to geometrical conditions. Thus by measuring the solute income in the acceptor it is possible to obtain a value proportional to the solute vapour tension. This permits calculation of all thermodynamic constants of the solution with an accuracy within the factor.

The apparatus will involve the sample investigated (the donor), the acceptor and a device for ensuring diffusion resistance in the gas phase. It should meet two requirements: the diffusion resistance must remain constant from experiment to experiment and should not exceed that of the donor or of the acceptor. In this case the rate of activity increase in the acceptor will be proportional to the vapour tension of the donor active constituent. Fig. 8 shows the kinetic curves for a 50 per cent silver–gold alloy.

The linear dependence of activity on time can be considered as a criterion for the fulfillment of the second requirement, since only in the gas phase does the diffusion resistance not change with time. To avoid

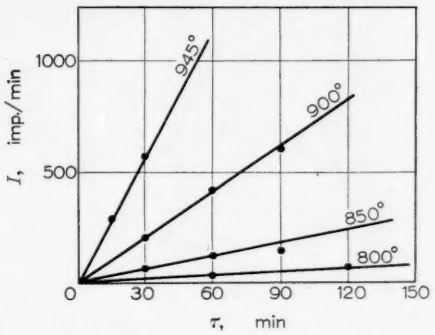

FIG. 8. Kinetic curves obtained by the diffusion method for an Ag–Cu alloy (N = 0·5).

difficulties connected with convection it would be feasible to use the capillary diffusion. If the rate of the substance transported from the donor into the acceptor were determined not by capillary but by surface diffusion, the method would give good results as to activity coefficients and heats of displacement, but would be inadequate for the determination of the heats of evaporation.

Let the rate of activity increase be denoted by v for the solution and by v_0 for the solvent.

The solute activity (a) will then be determined by v/v_0, and the heat of evaporation (λ) will be expressed by

$$\lambda = RT^2 \frac{d \ln v}{dT} + \frac{RT}{2} .$$

The second modification, the direct exchange method[10] is more readily realized. It resembles the Langmuir method. It is based on the fact that in the beginning of evaporation its rate is always lower than that of diffusion in the samples and consequently there always is a proportionality between I and t.

A disadvantage of this method is the possible effect of adsorbed layers, oxides, etc. blocking a part of the acceptor surface upon the evaporation rate. Hence the proportionality of I and t will only show that these inhibiting factors are independent of time.

The samples may be connected without an adapter, but be prepared as discs interlaid with sheets of mica. In determining

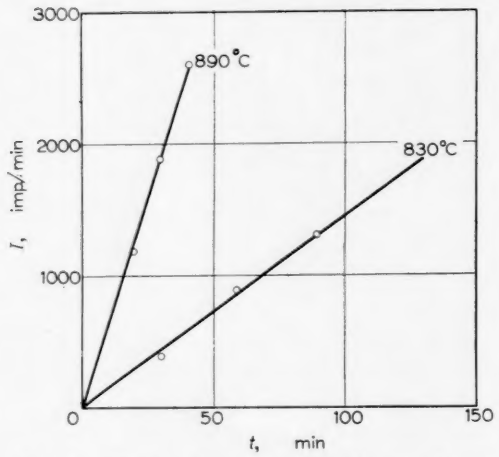

FIG. 9. Kinetic curves obtained by the direct exchange method (Ag).

the activity coefficient it would be useful to simultaneously anneal a couple of alloy samples and a couple of pure metals. This would reduce the possibility of errors connected with unstable temperature and different times of annealing. Fig. 9 shows kinetic curves for silver obtained by the direct exchange method at two different temperatures.

The method for determining the thermodynamic activity of solutes in liquid alloys worked out in collaboration with ZHURAVLEV[11] is approximate to the direct exchange method.

It is based on the fact that the amount of substance transported from the metal into some phase is proportional to its activity. The phase was represented by a cake of ZrO_2 with CaO as an additive. The cake was brought into contact with melted sulfur-containing iron and its activity was measured by a counter. The thermodynamic activity of the sulfur constituent was calculated from the obtained activity value, by comparing the latter with a standard activity .

The "coincidence method" permitting simultaneous measurements of the vapour tension and of the diffusion coefficient is perhaps most subject to errors.

BASILEVITCH gives a complete solution of the isotopic exchange problem by deriving the following expression for the overall activity of the acceptor

$$I = \frac{C_0 D}{\beta}\left\{\sqrt{\left(\frac{t\beta^2}{\pi D}\right)} + \frac{1}{4}\left[1 - \phi\left(2\sqrt{\left(\frac{t\beta^2}{D}\right)}\right)\right]\exp\frac{\beta^2}{4Dt} - \frac{1}{4}\right\}$$

where C_0 is the initial concentration of active atoms in the donor expressed in imp/cm^3; $\beta = (w/\rho)/w$ is the rate of evaporation, and ρ is the density.

By inserting dimensionless values for the time $t_1 = t\beta/D$ and for the distance $x_1 = x\beta/D$ the following relation can be obtained for the overall acceptor activity

$$A = \sqrt{\frac{t_1}{\pi}} + \frac{e^{4t_1}}{4}\left[1 - \phi\left(2\sqrt{t_1}\right)\right] - \tfrac{1}{4}$$

By plotting this universal dimensionless constant as $A = f(t_1)$ in a bilogarithmic plot it will always be possible to make coincide the experimental and dimensionless curves by shifting them in a direction parallel to their axes. As has been shown[10] both the vapour density and the diffusion coefficient can be determined from these shifts.

This technique is based on using the curvilinear part of the kinetic curve. Thus all the effects taking place during the experiment (such as oxidation, amorphization, smoking) will be recorded as erroneous characteristics, in the first place of the mobility effects.

The method described above, as well as those proposed by Langmuir and Knudsen, involves determination of the heat of dissolution as the difference in heats of evaporation. This leads to considerable errors, since a low value is determined as a difference in high values. The author together with GOLYTZYN[12] has worked out a technique based on the measurement of heats of dissolution, and also of equilibrium characteristics. It is free from the disadvantages of the "kinetic" methods.

It involves measurements of the heats of dissolution of the solid solute in the liquid solvent. The constituents of the latter should have a low solubility in the solid

substance, and the overall solubility of the solid body in the solvent should also be low.

As can be seen from published data silver meets these requirements with respect to the iron–carbon system.

The heat of dilution is determined from the difference in the heats of dissolution of γ-iron and austenite in liquid silver. The heat of dissolution was determined from measurements of the solubility of iron in silver as a function of the temperature.

To this means a 2 mm sample was suspended by a tungsten wire over a silica crucible (cross-section 6 mm) containing solid silver (99·999 per cent). The samples were prepared by alloying carbonyl iron (0·003 per cent of carbon) and synthetic cast iron with active Fe^{59} in a furnace with a carbon heater. Inactive samples were prepared simultaneously and analysed for carbon content.

After a vacuum of 5×10^{-5} mm Hg and a temperature of 1000–1100°C were attained the sample containing active iron was immersed in melted silver.

Special experiments have shown that complete saturation of the liquid solution with iron was obtained in 30 min.

In experiments using samples with a considerable carbon content the value for the solubility of iron in silver was not reproducible; it gradually increased for each portion of the solution approaching at last the true value. This was apparently due to lack of time for structural changes.

VINTAIKIN[13] has observed a similar effect on determining the heats of sublimation of iron and iron carbide alloys by the Knudsen method.

To avoid these errors each sample was subjected to reannealing for 15 min before immersion in silver.

The heats of dissolution of iron in silver were calculated from the slopes of the straight lines $\lg I - 1/T$.

As can be seen from Table 2 the maximum difference amounts to 1800 cal/mole. This corresponds to the value for the heat of austenite dilution in iron.

The mean square root deviation from the straight lines mentioned is 0·01, corresponding to 0·5 per cent in the determination of the plotted ordinate. The thermostatic errors are of the order of 1°, i.e. correspond to an error in the solubility value equal to 1 per cent. Thus the total error in the determination of heat will be less than 10 per cent. The total measured value for the heat of dilution is within experimental error but does not exceed 3000 cal/mole.

All the methods described have been verified experimentally and a considerable part of them were used in practice.

Results of the measurements of the silver diffusion coefficient by various methods at a temperature of 925°C are listed in Table 3.

TABLE 2. Heat of austenite dilution

C (per cent by weight)	Heat of dissolution (kcal/mole)
0·003	–33,800
1·68	–32,800
0·74	–34,600

TABLE 3. Self-diffusion coefficient of silver at 925°C

$D \times 10^9$ cm²/sec	Method used
3·0	Sectioning
3·7	Sectioning
3·7	Thin layer
3·3	Thick layer
3·5	Impression

The results of determination of self-diffusion in silver obtained by different authors at various temperatures are given in $\ln D - 1/T$ (Fig. 10).

The mean value for the activation energy obtained from curve $I = f(t)$ on the basis of the dimension theory is 45,900. This is consistent with the values obtained by JOHNSON[5] (45,950) and those determined by the thick layer method (45,000), by the

impression method (45,400), and by autoradiography (44,900).

Fig. 11 shows the self-diffusion coefficients

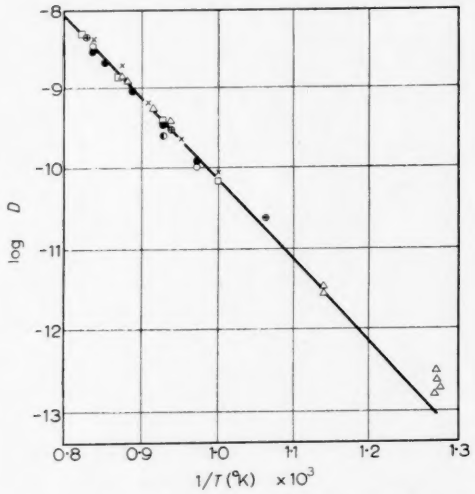

FIG. 10. Measurements of silver self-diffusion by various methods.
△ HOFFMAN and TURNBULL,[14] □ JOHNSON,[15] ⊕ SLIFKIN *et al.*,[16] × KRYUKOV and ZHOUKHOVITZKY, thin layer method,[2] ● ZHOUKHOVITZKY and GEODAKYAN, thick layer method,[1] ○ GEODAKYAN and ZHOUKOVITZKY, impression method,[3] ◑ ZHOUKHOVITZKY *et al.*[9]

of α and γ-iron determined by the impression method.

The results obtained are listed in Table 4.

The evidence obtained by the impression method for γ-iron is in good agreement with the most reliable results published.

The data obtained by various authors for α-iron differ considerably.

The error estimated *a priori* for diffusion coefficients determined by the method discussed is about 10 per cent. The actual error usually is some 5 per cent.

Experimental verification of the method for determining thermodynamic properties also gave positive results.

Fig. 12 shows the rate of increase with time in the activity of the silver acceptor (direct exchange method) as a function of the inverse temperature.

The calculated heat of evaporation (63,000) is in good agreement with the published results.

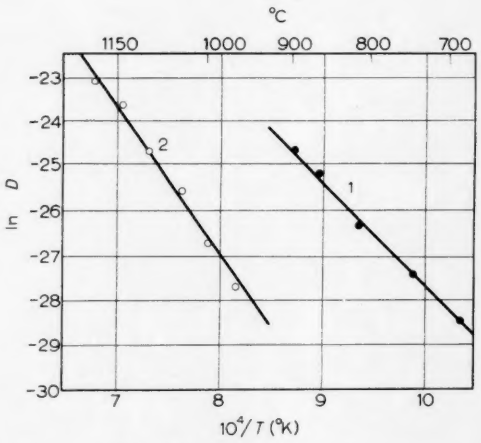

FIG. 11. Self-diffusion coefficients: for α-iron $D = 0{\cdot}019 \exp(-47{,}400/RT)$ (curve 1); for γ-iron $D = 1{\cdot}3 \exp(-67{,}900/RT)$ (curve 2) (impression method).

TABLE 4. Self-diffusion in iron

Temperature (°C)	D_0	E	Method used	Authors
715–910	$3{\cdot}4 \times 10^{-4}$	77,200	Absorption	BIRCHENALL, MEHL[17]
720–900	$2{\cdot}3 \times 10^{3}$	73,200	Absorption	BIRCHENALL, MEHL[17]
650–850	$5{\cdot}3 \times 10^{2}$	67,100	Thick layer	GOLIKOV, BORISOV[18]
705–850	0·14	52,000	Thin layer	KRYUKOV[2]
	0·11	48,000	Sectioning	GROUZIN[19]
700–890	0·02	47,400	Impression	GEODAKYAN[3]
910–1012	$1{\cdot}04 \times 10^{-3}$	48,000	Absorption	BIRCHENALL, MEHL[20]
970–1357	58·0	74,200	Absorption	BIRCHENALL, MEHL[20]
960–1250	0·76	68,000	Sectioning	GROUZIN[19]
960–1200	1·3	67,900	Impression	GEODAKYAN[3]

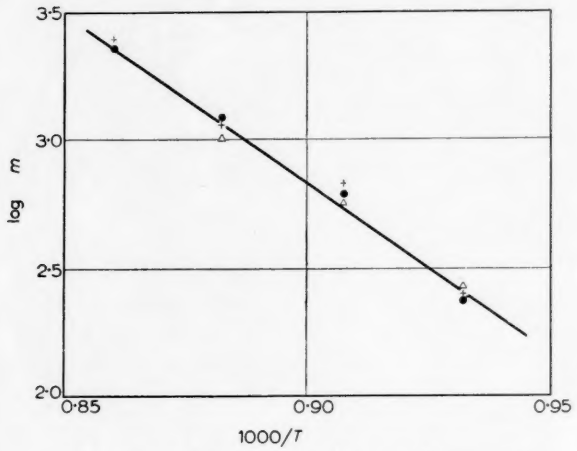

FIG. 12. Determination of the heat of evaporation of silver (direct exchange method).

Fig. 13 shows the sulfur activity coefficient in melted iron obtained by ZHURAVLEV at 1565°C (curve 1) and at 1670°C (curve 2) by the method discussed above, and by SHERMAN[21] (curve 3, $T = 1600$).

All the methods described can serve as an example of the possibilities opened up by the use of radioactive substances in investigations of various physico-chemical properties of substances.

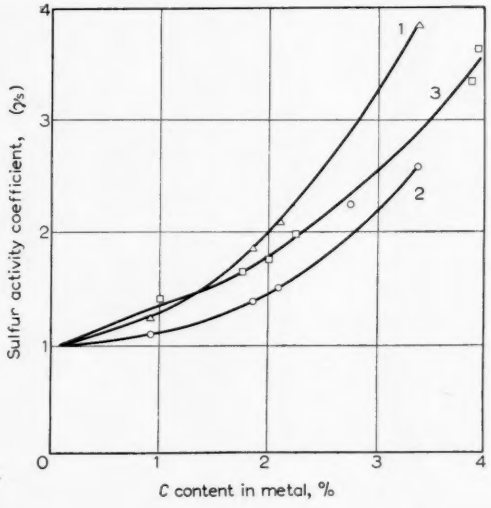

FIG. 13. Dependence of the activity coefficient of sulfur in liquid steel upon carbon content: 1 at 1565°C and 2 at 1670°C (data obtained by the author), 3 at 1600° (data obtained by S. Sherman).

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Méthodes d'Étude de l'Autodiffusion dans les Métaux à l'Aide des Radioisotopes

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L'utilisation des isotopes radioactifs a permis de définir avec une précision croissante les coefficients d'autodiffusion dans les métaux. Cet article traite des différentes méthodes actuellement utilisées dans ce but, tant en ce qui concerne l'autodiffusion en volume que l'autodiffusion intergranulaire. Le choix des méthodes est maintenant assez étendu, dans le cas de l'autodiffusion massique. La méthode de sectionnement est sans doute la plus précise, mais elle est pratiquement limitée à la mesure de coefficients de diffusion supérieurs à 10^{-11}. Les coefficients plus faibles doivent être déterminés à l'aide de méthodes d'absorption; dans ce cas, le choix de la méthode pour résoudre un problème donné dépend surtout des caractéristiques des rayonnements émis par les isotopes radioactifs. Nous passons en revue les différentes méthodes d'absorption récemment utilisées, en illustrant chacune d'elles par un exemple concret; nous avons porté un intérêt particulier aux méthodes qui, par une fixation judicieuse des paramètres géométriques, permettent d'éliminer la connaissance des caractéristiques d'absorption des rayonnements.

L'étude de l'autodiffusion intergranulaire présente un choix plus restreint de méthodes; nous avons insisté sur la comparaison entre les valeurs de la concentration dans les joints de grains que donnent les théories de Fisher et Whipple et précisé dans quelles conditions la formule de Fisher, d'application simple, permet d'appliquer à la diffusion intergranulaire la méthode de sectionnement.

METHODS OF STUDYING SELF-DIFFUSION IN METALS BY MEANS OF RADIOISOTOPES

The use of radioactive isotopes has enabled self-diffusion coefficients in metals to be determined with progressively greater accuracy. This paper deals with the different methods in use at present for studying both general self-diffusion and inter-granular self-diffusion. There is now a fairly wide choice of methods for general self-diffusion; that of examining sections is undoubtedly the most accurate, but in practice it is limited to the measurement of diffusion coefficients greater than 10^{-11}. For smaller values, absorption methods must be employed; in that case, the choice of method for solving a given problem depends above all on the radiation characteristics of the radioactive isotopes. The various absorption methods which have been used recently are examined, each one being illustrated by a specific example; particular emphasis has been laid on those methods in which careful choice of the geometric parameters eliminates the need to know the absorption characteristics of the radiations.

The choice of methods for studying intergranular self-diffusion is more limited; comparison of the values of concentration in the grain boundaries given by the theories of Fisher and of Whipple, respectively, is given prominence, and conditions are defined under which, by a simple application of Fisher's formula, the sectional method may be used to examine intergranular diffusion.

МЕТОДЫ ИССЛЕДОВАНИЯ САМОИЗЛУЧЕНИЯ В МЕТАЛЛАХ РАДИОИЗОТОПАМИ

Употребление радиоактивных изотопов дало возможность определять коэффициент саморассеяния в металлах все с большей и большей аккуратностью. Эта статья описывает различные методы, употребляемые в настоящее время для изучения, как общего саморассеяния так и меж-зернистого саморассеяния. В настоящее время имеется довольно обширный выбор методов саморассеяния; способ, употребляемый для исследования частиц, несомненно является самым аккуратным, но на практике это ограничивается измерением коэффициента саморассеяния величин больше 10^{-11}. Для меньших величин должны применяться способы абсорбции; в коем случае, выбор метода для разрешения представленной задачи, зависит главным образом от характеристики излучения радиоактивного изотопа. Изучались различные, применяемые недавно способы, каждый был иллюстрирован специальным примером; особенно были подчеркнуты те методы в которых тщательный выбор геометрических параметров, исключает необходимость знать характеристику поглощения излучений.

Для исследования меж-зернистого саморассеяния имеется более ограниченный выбор методов; в теориях Фишера и Виппл выдающееся место отведено сравнению величины концентрации в пределах зерна, и описаны условия согласно которым, простым применением формулы Фишера, секционный метод может применяться для исследования меж-зернистого рассеяния.

METHODEN ZUM STUDIUM DER SELBSTDIFFUSION IN METALLEN MIT HILFE VON RADIO-ISOTOPEN

Die Verwendung von Radioisotopen gibt die Möglichkeit den Koeffizienten der Selbstdiffusion in Metallen mit zunehmender Genauigkeit zu definieren. Dieser Artikel behandelt verschiedene, bereits verwendete Methoden soferne sie sich auf Selbstdiffusion im ganzen Volumen und auf Selbstdiffusion on Korngrenzen beziehen. Die Wahl der Methode im Falle der Massen-Selbstdiffusion ergibt sich zwangsläufig. Die Methode Schnitte herzustellen ist zweifellos die genaueste, jedoch beschränkt sie sich in der Praxis auf die Messung von Diffusionskoeffezienten grösser als 10^{-11}. Schwächere Koeffizienten müssten mit Hilfe der Absorptionsmethode bestimmt werden; in diesem Fall ergibt sich die Wahl der Methode zur Lösung des Problems je nach den Eigenschaften der Strahlung des jeweils verwendeten Radio-Isotops. Es wird ein Überblick gegeben über die verschiedenen neuerdings verwendeten Absorptionsmethoden, wobei jede einzelne durch ein konkretes Beispiel belegt wird. Dabei wurde besonders Wert auf jene Methoden gelegt, bei welchen durch vernünftige Festsetzung der geometrischen Parametere die Kenntnis der Absorptionseigenschaften der jeweiligen Strahlung überflüssig wird.

Untersuchung der intergranularen Selbstdiffusion bedeutet eine Einschränkung in der Wahl der Methoden. Es wurde besonders Wert darauf gelegt die Konzentrationswerte an den Korngrenzen mit denen nach den Theorien von Fisher und von Whipple zu vergleichen und konnte unter bestimmten Bedingungen die Formel von Fisher bestätigen, die in einfacher Anwendung die Schnittmethode auf die intergranulare Diffusion zu verwenden gestattet.

INTRODUCTION

De nombreuses méthodes expérimentales permettent d'étudier la diffusion intermétallique. En effet, l'introduction d'un élément *B* dans le réseau d'un élément *A* entraîne une variation de pratiquement toutes les propriétés physiques de *A*. Si l'on sait mesurer avec suffisamment de précision les variations d'une de ces propriétés, il devient possible d'étudier facilement la pénétration de *B* dans *A*, donc d'aborder les problèmes de diffusion. Les variations de sensibilité à l'attaque chimique, de dureté, d'intensité des rayons X de fluorescence etc . . . ont ainsi pu être mises à profit. Il n'en est plus de même si l'on envisage le problème de l'autodiffusion, c'est-à-dire le déplacement des atomes de *A* dans la masse de *A* sous l'action de l'agitation thermique. On a mis au point un certain nombre de méthodes indirectes comme le frittage ou la mesure du grossissement des grains. Leur principal inconvénient est d'ordre logique: en effet, elles ne prennent leur sens que lorsque, dans un

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certain nombre de cas, on parvient à établir une correspondance entre leurs résultats et ceux que l'on a pu établir directement. Pratiquement, les méthodes utilisant les isotopes radioactifs représentent le seul moyen d'étudier directement les problèmes que pose l'autodiffusion. Leur principe est bien connu; avec une très bonne approximation, les atomes d'un élément radioactif se comportent comme les atomes inertes correspondants. Pour effectuer une expérience d'autodiffusion, il suffit donc de déposer une couche d'isotopes radioactifs à la surface d'un échantillon inactif; l'étude de la répartition du radioélément après un recuit convenable permet de remonter à la connaissance des paramètres de diffusion.

Il ne saurait être question, dans cet article, d'envisager tous les aspects expérimentaux que l'on rencontre dans une expérience de diffusion. Nous souhaitons simplement rassembler un certain nombre de résultats montrant quelle méthode il y a lieu de choisir quand on se trouve en présence d'un problème déterminé d'autodiffusion. Nous adopterons l'ordre naturel de telles recherches:

(1) résolution des équations de la diffusion et choix des conditions expérimentales imposées par leur formalisme.

(2) modifications entrainées par les caractéristiques *physiques* des éléments radioactifs utilisés.

Nous donnerons, dans chaque cas intéressant, un exemple précis, en essayant d'insister sur les limites expérimentales. En fait, le nombre d'expériences suggérées par le calcul est beaucoup plus vaste, comme on pourra le constater en consultant l'important ouvrage de CRANK.[1]

1. LES ÉQUATIONS DE LA DIFFUSION ET LEUR RESOLUTION

Si la diffusion s'effectue *dans une seule direction*, x, le transport de matière est, dans le cas de l'autodiffusion, régi par l'équation de Fick:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (1.1)$$

c étant la concentration, t le temps, D le coefficient de diffusion. Ce dernier est lié à la température absolue, T, par une relation d'Arrhénius:

$$D = D_0 \exp(-Q/RT) \qquad (1.2)$$

R étant la constante des gaz parfaits. D_0 est appelé facteur de fréquence et Q énergie d'activation.* La connaissance de D_0 et Q renseigne sur la facilité d'un phénomène donné de diffusion. Le but des mesures est donc la détermination de D_0 et Q. Q s'exprime généralement en calories/atome-gramme et D_0 en cm²/sec. Signalons que l'équation (1.1) n'est pas en général applicable aux problèmes de l'hétérodiffusion, car alors D_0 dépend de la concentration.

Deux remarques s'imposent immédiatement:

(1) l'équation (1.1) est la même que l'équation de conduction de la chaleur dans un milieu homogène. Il sera donc possible, dans de nombreux cas, d'établir des analogies utiles entre les deux phénomènes de transport de la chaleur et de transport de la matière.

(2) elle ne serait rigoureuse que si l'on pouvait étudier le déplacement des atomes *eux-mêmes*. En réalité, on s'intéresse au mouvement d'atomes radioactifs dans un milieu inactif. Il peut donc exister un effet de masse, d'autant plus important que l'on étudie des éléments plus légers. Nous le négligerons dans la suite de cet exposé, mais il est bon de connaître une telle possibilité.

L'équation de Fick n'a pas de solution unique. Pour la résoudre, il est nécessaire de connaître:

(1) les *conditions initiales*, fixant l'état du système étudié avant tout traitement de diffusion ($t = 0$)

(2) les *conditions aux limites*, tenant compte:

(a) de facteurs géométriques imposés par les conditions de l'expérience.

* Q est en général compris entre 10 et 80 kcal/at. g. D_0 est très variable, mais souvent compris entre 0,1 et 10 cm²/sec

(b) de facteurs physiques liés à la nature même du phénomène de diffusion (par exemple, conditions de continuité).

Une fois la résolution effectuée, il est nécessaire de vérifier l'unicité de la solution obtenue. Il s'agit ici de calculs, en général très délicats, que nous ne traiterons pas ici. Nous admettrons donc que, dans chaque cas traité, nous serons parvenus à décrire formellement le phénomène de diffusion sans effectuer les vérifications aux limites. On pourra se reporter à l'ouvrage classique de CARSLAW et JAEGER[2] sur la transmission de la chaleur si l'on désire trouver quelques exemples de vérification d'unicité des solutions.

La forme de l'équation de Fick montre qu'elle est redevable des méthodes du calcul opérationnel. Cependant, nous n'aborderons pas ici les techniques de transformation qui, malgré leur souplesse et leur puissance, ne sont pas nécessaires à la résolution du problème, relativement simple, de la diffusion intermétallique.

1.1. Méthode de superposition

Soit un cylindre infini (Fig. 1), de section unité. Nous supposons qu'au temps $t = 0$, on introduit dans le plan $x = 0$ une quantité

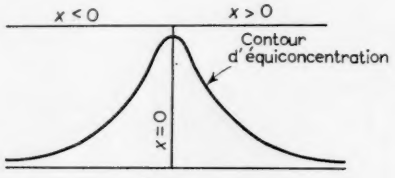

FIG. 1.

Q de substance diffusante, parfaitement répartie dans toute la section et qu'il n'y a pas de pertes de substance au cours des expériences (par exemple, que l'évaporation est négligeable).

L'équation (1.1) est vérifiée par toute expression de la forme:

$$c = \frac{k}{\sqrt{t}} \exp\,(-x^2/4Dt)$$

La quantité totale de substance diffusante, à un instant quelconque, doit être égale à Q. Donc:

$$Q = \int_{-\infty}^{+\infty} \frac{k}{\sqrt{t}} \exp\,(-x^2/4Dt)\,dx$$

Posons:

$$\xi^2 = x^2/4Dt; \quad d\xi = dx/2\sqrt{(Dt)}$$

On a:

$$Q = 2k\sqrt{D} \int_{-\infty}^{+\infty} \exp\,(-\xi^2)\,d\xi = 2k\sqrt{(\pi D)}$$

d'où:

$$k = Q/2\sqrt{(\pi D)}$$

Il en résulte que le phénomène peut se décrire par l'expression

$$c = (Q/2\sqrt{(\pi Dt)}) \exp\,(-x^2/4Dt) \quad (1.1.1)$$

Le même raisonnement, appliqué au cas d'un cylindre semi-infini ($x \geqslant 0$) donne:

$$c = (Q/\sqrt{(\pi Dt)}) \exp\,(-x^2/4Dt) \quad (1.1.2)$$

équation particulièrement importante dans la pratique. Tout se passe comme si la substance qui, dans un cylindre infini, aurait diffusé dans la région $x < 0$ s'était réfléchie sur une paroi imperméable placée à l'abscisse $x = 0$. Cette remarque constitue le *principe de réflexion.*

Si, au lieu d'une couche infiniment mince, on envisage la diffusion d'une bande étendue, il est possible de traiter le problème d'une manière analogue en assimilant la bande à une succession de sources infiniment minces (*principe de superposition*).

Nous en donnerons un exemple simple. Soit un cylindre semi-infini ($x \geqslant 0$) auquel on accole, au temps $t = 0$, un cylindre de même section et également semi-infini ($x < 0$) (Fig. 2). Etudions la variation de

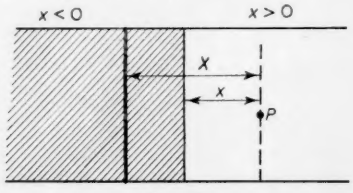

FIG. 2.

concentration en un point P de la masse métallique. Considérons dans la région $x < 0$ une bande de largeur dX prise à la distance X du point P.

Si la concentration de substance diffusante est dans la région $x < 0$ égale à c_0 par

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unité de volume, la quantité de matière localisée dans la bande dX est: $c_0\,dX$. Cette bande crée donc, au point P, une concentration donnée par (1.1.1):

$$c = (c_0\,dX/2\sqrt{(\pi Dt)})\exp(-X^2/4Dt)$$

Si nous supposons maintenant l'action de toutes les bandes de largeur dX isolables dans la région $x < 0$, on a:

$$c = \frac{c_0}{2\sqrt{(\pi Dt)}}\int_x^\infty \exp(-X^2/4Dt)\,dX$$

Posons:

$$\xi^2 = x^2/4Dt;\ d\xi = dX/2\sqrt{(Dt)}$$

$$c = (c_0/\sqrt{\pi})\int_{x/2\sqrt{(Dt)}}^\infty \exp(-\xi^2)\,d\xi = c_0/\sqrt{\pi}$$

$$\times\left[\int_0^\infty \exp(-\xi^2)\,d\xi - \int_0^{2/2\sqrt{(Dt)}} \exp(-\xi^2)\,d\xi\right]$$

$$= (c_0/\sqrt{\pi})\{\sqrt{\pi}/2 - \operatorname{erf}[x/2\sqrt{(Dt)}]\}$$

en posant:

$$\operatorname{erf}(\eta) = (2/\sqrt{\pi})\int_0^\eta \exp(-\xi^2)\,d\xi \quad (1.1.3)$$

Donc:

$$c = (c_0/2)\{1 - \operatorname{erf}[x/2\sqrt{(Dt)}]\}$$
$$= (c_0/2)\operatorname{erfc}[x/2\sqrt{(Dt)}]$$

Le même raisonnement permet de traiter le cas où, à l'instant t, la substance diffusante est comprise entre les plans $x = +h$ et $x = -h$ (Fig. 3). L'intégration sur les x

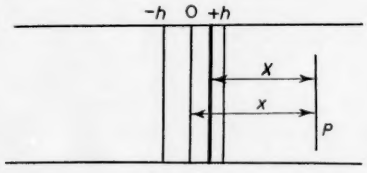

FIG. 3.

doit alors s'effectuer de $(x - h)$ à $(x + h)$. On obtient alors:

$$c = (c_0/2)\{\operatorname{erf}[(h - x)/2\sqrt{(Dt)}] + \operatorname{erf}[(h + x)/2\sqrt{(Dt)}]\} \quad (1.1.4)$$

Cette expression est évidemment valable dans le cas d'un cylindre semi-infini.

Tous les problèmes de diffusion peuvent se traiter par cette méthode de superposition. Malheureusement, on arrive très rapidement à des calculs très longs. On est obligé alors de faire appel à d'autres méthodes, parmi lesquelles nous citerons la méthode de séparation des variables.

1.2. Méthode de séparation des variables

Soit à résoudre l'équation de Fick:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Supposons que c puisse s'exprimer sous la forme du produit d'une fonction du temps $T(t)$ par une fonction de x, $X(x)$. Dans ce cas:

$$c = T(t)\cdot X(x)$$

$$\frac{\partial c}{\partial t} = X(x)\cdot\frac{\partial T(t)}{\partial t}$$

$$\frac{\partial^2 c}{\partial x^2} = T(t)\cdot\frac{\partial^2 X(x)}{\partial x^2}$$

Alors:

$$X(x)\frac{\partial T(t)}{\partial t} = DT(t)\frac{\partial^2 X(x)}{\partial x^2}$$

soit:

$$\frac{1}{T}\frac{\partial T}{\partial t} = \frac{D}{X}\frac{\partial^2 X(x)}{\partial x^2} = K,$$

K étant une constante, puisque la relation précédente doit être vérifiée pour toutes les valeurs de t et de x. On peut écrire, sans nuire à la généralité du problème $K = -\lambda^2 D$; λ devient alors un paramètre.

$$\frac{1}{T}\frac{\partial T}{\partial t} = -\lambda^2 D$$

donne:

$$T = \exp(-\lambda^2 Dt)$$

et:

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\lambda^2$$

$$X = A\sin\lambda x + B\cos\lambda x$$

d'où:

$$c = (A\sin\lambda x + B\cos\lambda x)\exp(-\lambda^2 Dt)$$

Il est évident que λ peut prendre toutes les valeurs possibles. On peut donc écrire:

$$c = \sum_{n=0}^{\infty}(A_n\sin\lambda_n x + B_n\cos\lambda_n x) \times \exp(-\lambda_n{}^2\,Dt)$$

qui est la solution la plus générale du problème. A_n, B_n, et λ_n sont déterminés par les conditions du problème considéré.

Nous citerons un exemple d'application de la méthode, exemple que nous examinerons plus loin d'un point de vue pratique.

Soit une bande métallique de largeur l. Déposons à sa surface un dépôt de métal diffusant d'épaisseur h (Fig. 4). Comme il

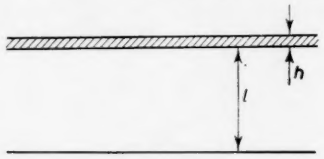

FIG. 4.

ne doit pas y avoir diffusion dans le milieu extérieur:

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \left(\frac{\partial c}{\partial x}\right)_{x=l} = 0$$

Donc: puisque,

$$\frac{\partial c}{\partial x} = \sum_1^\infty \lambda_n (A_n \cos \lambda_n x - B_n \sin \lambda_n x) \times \exp(-\lambda_n{}^2 Dt),$$

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = 0 \quad \text{entraîne} \quad A_n = 0$$

et:

$$\left(\frac{\partial c}{\partial x}\right)_{x=l} = 0; \quad B_n \sin \lambda_n l = 0,$$

soit:

$$\lambda_n l = n\pi$$

ou:

$$\lambda_n = n\pi/l$$

On a ainsi pu donner à λ_n une forme simple faisant intervenir directement un paramètre n.

La concentration dans la bande est donc donnée par:

$$c = \sum_{n=0}^{\infty} B_n \cos \frac{n\pi x}{l} \exp\left(-\frac{n^2\pi^2}{l^2} Dt\right)$$

Si $t = 0$,

$$c = \sum_0^\infty B_n \cos \frac{n\pi x}{l}$$

Or, la distribution initiale de substance diffusante est facile à développer en série de Fourier. On trouve:

$$c = c_0 \left[\frac{h}{l} + \frac{2}{\pi} \sum_1^\infty \frac{1}{n} \sin \frac{n\pi h}{l} \cos \frac{n\pi x}{l}\right]$$

d'où

$$B_n = \frac{2}{n\pi} \sin \frac{n\pi h}{l}$$

Finalement:

$$c = c_0 \left[\frac{h}{l} + \frac{2}{\pi} \sum_1^\infty \frac{1}{n} \exp\left(-\frac{n^2\pi^2 Dt}{l_2}\right) \times \cos \frac{n\pi x}{l} \sin \frac{n\pi h}{l}\right]$$

Cette expression se simplifie si l'on suppose que $h \ll l$.

Alors:

$$c = c_0 \frac{h}{l} \left[1 + 2 \sum_1^\infty \frac{\cos n\pi x}{l} \cdot \frac{1}{n} \cdot \times \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right)\right] \quad (1.2.2)$$

Si, de plus, on attend suffisamment longtemps pour qu'on puisse se limiter au premier terme du développement, on trouve:

$$c = c_0 \frac{h}{l} \left[1 + 2 \cos \frac{\pi x}{l} \exp\left(-\frac{\pi^2 Dt}{l^2}\right)\right] \quad (1.2.3)$$

C'est sous cette forme que nous utiliserons l'équation par la suite.

2. RAPPEL DES PROPRIÉTÉS DES RAYONNEMENTS β ET γ

Avant d'aborder l'étude des méthodes expérimentales, il est utile de rappeler certaines caractéristiques des rayonnements β et γ qui détermineront les limites d'utilisation de telle ou telle méthode.

2.1. Les rayonnements β

Les rayonnements β étant de nature corpusculaire, de spectre énergétique continu, il n'y a *a priori* aucune raison pour que leur absorption obéisse à la loi exponentielle de Beer–Lambert. Néanmoins, il arrive souvent, par une combinaison des facteurs de l'absorption, que l'on puisse décrire avec une bonne approximation l'absorption par une relation exponentielle. Mais ce

n'est pas toujours le cas et il est indispensable de vérifier la validité de la loi exponentielle, surtout si le radioélément utilisé émet plusieurs rayonnements β.

2.2. Les rayonnements γ

Les rayonnements γ, de nature électromagnétique, sont beaucoup moins absorbés par la matière et obéissent à la loi de Beer–Lambert. Ceci n'est vrai en toute rigueur que lorsque le radioélément n'émet qu'un seul rayonnement γ. Sinon, comme l'ont montré JAUMOT et SMITH,[3] il faut faire une étude détaillée de l'absorption, ce qui peut conduire à des difficultés dans l'interprétation des résultats comme nous le verrons plus loin.

2.3. Détection des rayonnements β et γ

En dehors des techniques classiques de comptage, on tend de plus en plus à utiliser pour l'étude de l'autodiffusion la technique autoradiographique. Il faut rappeler que si l'on applique sur une émulsion photographique une source radioactive émettant à la fois des rayons β et γ, l'absorption plus grande des rayons β se traduit par un noircissement localisé, alors que les rayons γ donnent plutôt un fond continu. La tendance actuelle est d'accroître le pouvoir de résolution des images autoradiographiques, en utilisant par exemple des émulsions très fines détachables d'un support rigide ("stripping films") ou des émulsions que l'on coule sur l'échantillon radioactif (méthode de TOWE *et al.*[4])

3. LES MÉTHODES EXPÉRIMENTALES D'ÉTUDE DE L'AUTODIFFUSION EN VOLUME

3.1. La méthode de sectionnement

3.1.1. Principe. La méthode de sectionnement est sans doute la plus utilisée dans les études consacrées à l'autodiffusion. Malgré ses difficultés d'utilisation, elle présente le gros avantage de ne pas nécessiter la prise en considération des caractéristiques des rayonnements. Elle est donc sûre et d'une interprétation simple. Elle permet également, comme nous le verrons plus loin, d'aborder des problèmes plus métallurgiques comme la structure des joints de grains.

Elle repose sur la réalisation expérimentale des conditions aux limites imposées par l'équation (1.1.2). A la surface d'un échantillon suffisamment épais (quelques mm) pour qu'il puisse être assimilé à un milieu semi-infini, on dépose une couche d'isotopes radioactifs. Cette couche doit être *très mince* (quelques microns au maximum), pour que l'équation (1.1.2) soit valable. Le dépôt peut s'obtenir par électrolyse, par vaporisation sous vide etc. . . . On effectue ensuite le recuit de diffusion sous vide ou en atmosphère contrôlée. La température de recuit doit être connue à moins de 1° près. Après recuit, on abrase les faces latérales de l'échantillon pour supprimer les effets de surface. On pratique alors une série de sectionnements, en retirant à chaque fois quelques centièmes de mm. On détermine, après chaque sectionnement, l'épaisseur enlevée par pesée ou par mesure de l'avance de l'outil de coupe. On récupère soigneusement toutes les particules arrachées. On peut alors, soit les dissoudre dans un acide, soit les fondre, soit les redéposer par électrolyse après dissolution. La mesure de l'activité de chaque section permet de connaître, à un facteur près imposé par les conditions géométriques du comptage, à l'absorption des rayonnements par la solution acide utilisée dans le cas où l'on effectue des dissolutions, la concentration en atomes radioactifs dans chaque section. L'équation (1.1.2) montre que si l'on porte le logarithme népérien de l'activité mesurée en fonction du carré de la profondeur des sections, on doit obtenir une droite de pente $-\frac{1}{4}Dt$. En répétant les expériences à différentes températures, on en déduit les valeurs de D_0 et Q.

3.1.2. Précision de la méthode. La méthode de sectionnement est commode, car elle ne nécessite pas la connaissance des caractéristiques d'absorption des rayonnements. Les

plus grandes difficultés sont d'ordre expérimental.

3.1.2.1. L'erreur sur le temps de recuit est négligeable si l'on prend soin d'introduire rapidement les échantillons dans un four porté à la température de recuit et si on peut les tremper rapidement, une fois le recuit terminé. Le mieux est sans doute de sceller les échantillons dans des tubes de silice, dont la manipulation est relativement simple.

3.1.2.2. La précision sur les comptages est facilement de 2 pour cent, compte tenu de l'erreur statistique (1 pour cent si on compte 10^4 impulsions) et de la non-reproductibilité des conditions géométriques.

3.1.2.3. Une erreur plus importante peut s'introduire dans la détermination des épaisseurs enlevées. Il faut évidemment être sûr de récupérer toutes les poussières arrachées de l'échantillon. Mais cette opération effectuée, il faut peser les particules. Si p est le poids mesuré, ε l'épaisseur et d le diamètre de l'échantillon, on a:

$$\Delta\varepsilon/\varepsilon = \Delta p/p + 2\Delta d/d.$$

L'erreur relative sur la connaissance de d est faible. Pour que les mesures aient un sens, il est nécessaire que $\Delta p/p$ ne soit pas supérieur à 2 pour cent. Comme on ne peut espérer, avec une bonne balance de laboratoire, avoir une erreur inférieure à 0,1 mg, il est nécessaire que p soit d'environ 5 mg. Si nous supposons que $d = 1$ cm et que la densité du métal est égale à 8, on voit que ε doit être d'une dizaine de microns au minimum. Ceci limite l'intérêt de la méthode de sectionnement dans le cas où la diffusion n'a progressé que sur une très faible épaisseur.

3.1.2.4. Le mode de découpage peut également introduire une erreur. Il est en effet nécessaire que les épaisseurs enlevées soient effectivement *parallèles* au front de diffusion. Shirn *et al.*[5] ont essayé de chiffrer cette erreur. Si l'on suppose que l'échantillon est un cylindre de diamètre d, que l'on y découpe des lamelles d'épaisseur ε et que α est l'angle d'inclinaison de l'axe de l'éprouvette par rapport à l'axe d'usinage, on montre que la pente de la droite $\log c = f(x^2)$ est en réalité égale à:

$$-(1/4Dt)[1 - (\varepsilon^2 + 3d^2\alpha^2/4)/24Dt].$$

L'erreur relative sur la connaissance de la pente est donc égale à:

$$(\varepsilon^2 + 3d^2\alpha^2/4)/24Dt$$

Si l'on suppose que $D = 10^{-9}$ cm²/sec, $t = 10^5$ sec (environ 30 hr), $d = 1$ cm, $\varepsilon = 10^{-3}$ cm, $\alpha = 0{,}5°$, on trouve que l'erreur sur la pente est d'environ 2 pour cent. Par contre, elle atteint 8 pour cent si $\alpha = 1°$. On voit donc l'importance du contrôle de l'angle d'attaque de l'échantillon. On peut évidemment diminuer cette erreur en diminuant la dimension transversale de l'éprouvette. Mais la précision sur la connaissance de l'épaisseur enlevée en devient d'autant plus faible.

3.1.3. Réalisation expérimentale et limites d'utilisation. On trouvera dans la littérature de nombreux exemples d'application de la méthode de sectionnement. Nous ne ferons que mentionner certaines solutions préconisées pour en accroître la précision.

3.1.3.1. La plupart du temps, les sectionnements s'effectuent à l'aide d'un outil en acier spécial monté sur un tour d'horlogerie. Les poussières et copeaux sont récupérés dans un manchon entourant la machine. Il est préférable de peser les copeaux plutôt que la partie restante de l'échantillon, de manière à conserver la position de ce dernier par rapport à l'outil. Makin *et al.*[6] ont préféré mesurer les épaisseurs enlevées à l'aide d'un comparateur fixé sur le tour.

3.1.3.2. Liu et Drickamer[7] ont essayé de tourner la difficulté d'emploi d'une machine de précision en effectuant des abrasions sur du papier émeri et en passant ensuite les différents papiers sous un compteur de Geiger. La méthode n'a évidemment d'intérêt que si la profondeur de pénétration est assez grande.

3.1.3.3. Pour accroître les possibilités de la méthode vers la mesure des faibles coefficients de diffusion, Neiman et Chinaev[8] ont effectué les sectionnements par dissolution électrolytique. Après chaque dissolution, on mesure l'activité de la solution.

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La méthode est tributaire de la possibilité d'obtenir par dissolution des surfaces bien planes.

La méthode de sectionnement est limitée par son principe même. Pour tracer la courbe $\log c = f(x^2)$ avec suffisamment de précision, il est nécessaire que la pénétration limite du radioélément (que nous pouvons définir arbitrairement comme la distance à laquelle l'activité est égale à une fraction donnée de l'activité du dépôt initial) soit assez grande devant l'épaisseur des couches retirées. Si l'on parvient à découper des tranches de 20 μ d'épaisseur, la pénétration doit être d'au moins 100 μ. Il est facile de montrer que, dans ces conditions, on ne pourra pas mesurer un coefficient de diffusion *inférieur à* 10^{-11}, pour un temps de recuit égal à 10^6 sec (environ 12 jours). L'augmentation du temps de recuit ne modifie d'ailleurs que lentement la limite inférieure des coefficients de diffusion mesurables.

En résumé, la méthode de sectionnement est précise, à condition de définir très rigoureusement ses conditions géométriques, mais dans les conditions normales d'emploi, elle ne permet pas de mesurer des coefficients de diffusion $<10^{-11}$. Cela suffit à la rendre inopérante dans un certain nombre de cas (fer α, par exemple). Elle offre par contre un intérêt considérable dans l'étude de la diffusion intergranulaire (voir plus loin).

3.1.4. La méthode de dissolution de Geodakyan et Zhoukhovitzky. Nous rattacherons à la méthode de sectionnement celle récemment mise au point par GEODAKYAN et ZHOUKHOVITZKY.[9] Si nous supposons que x est infiniment petit dans l'équation (1.1.2), on a:

$$c = Q/\sqrt{(\pi Dt)}$$

Si l'on parvient à tracer la courbe $c/Q = f(1/\sqrt{t})$, on trouve une droite de pente $1/\sqrt{(\pi D)}$. La méthode revient donc à étudier la variation de l'activité du dépôt initial. Geodakyan et Zhoukhovitzky donnent comme exemple d'application l'étude de l'autodiffusion du fer γ. Une feuille de papier filtre imprégnée d'une solution de ClNa est pressée entre une cathode et l'échantillon qui joue le rôle d'anode. On fait passer un courant de 20 μA pendant 3–5 min. On mesure alors l'activité du papier, qui est caractéristique de l'activité superficielle. En effet, la durée d'électrolyse est insuffisante pour dissoudre une épaisseur importante de fer. La méthode a été depuis perfectionnée par une forte augmentation de l'intensité, ce qui entraîne une forte diminution du temps d'électrolyse.* Elle permet de mesurer en quelques heures de recuit de très faibles coefficients de diffusion (10^{-14}). C'est sans doute à l'heure actuelle la méthode la plus rapide. D'après les auteurs, la précision n'est pas très bonne mais cet inconvénient est compensé par la rapidité des expériences. Il faut signaler que, dans le cas de l'étude des métaux oxydables, il est nécessaire d'éviter les scellements (trop longs à réaliser), mais néanmoins de trouver un moyen de protéger l'échantillon (pompage continu). D'autre part, les recuits étant très courts, il faut amener directement l'échantillon en température. La grosse difficulté de la méthode semble donc être la connaissance précise du temps de recuit, alors que ce dernier est effectué sous vide dynamique. La méthode a servi à étudier l'autodiffusion du fer et de l'argent.

3.2. Les méthodes d'absorption

Depuis quelques années, le nombre des méthodes d'absorption est devenu assez important. Ce développement est dû aux limites de la méthode de sectionnement et à l'intérêt de mesurer de faibles coefficients de diffusion. Toutes ont le même principe: on effectue un dépôt radioactif à la surface d'un bloc métallique, et on mesure, au cours du temps, la variation de l'activité globale de tout l'échantillon. Si l'on connait la loi d'absorption des rayonnements, on peut en déduire le coefficient de diffusion.

3.2.1. La méthode de décroissance simple. Elle est due à STEIGMAN *et al.*[10] Si l'on effectue un dépôt mince à la surface d'un

* A. A. ZHOUKHOVITZKY, Communication privée.

échantillon considéré comme semi-infini, la concentration en radioélément à la distance x est donnée par l'équation

$$c = (Q/\sqrt{(\pi Dt)}) \exp(-x^2/4Dt) \quad (1.1.2)$$

Considérons une bande infiniment mince de largeur dx, dans laquelle la concentration est constante et égale à la valeur précédente; cette bande est prise à la distance x du dépôt. Si nous supposons que l'absorption des rayonnements est exponentielle, la bande élémentaire va apporter à l'activité totale une contribution:

$$c = (Q/\sqrt{(\pi Dt)}) \exp(-x^2/4Dt) \exp(-\mu x)\, dx,$$

μ étant le coefficient d'absorption.

En mesurant l'activité totale de l'échantillon, A, on obtient une valeur:

$$A = K \int_0^\infty \frac{Q}{\sqrt{\pi Dt}} \exp - \left(\frac{x^2}{4Dt} + \mu x\right) dx,$$

K étant un facteur de comptage.
Posons

$$\xi = \frac{x}{2\sqrt{(Dt)}} + \mu\sqrt{(Dt)};$$

on obtient:

$$A = \frac{KQ}{\sqrt{(\pi Dt)}} \exp(\mu^2 Dt) \int_{\mu\sqrt{(Dt)}}^\infty \exp(-\xi^2)\, d\xi$$

$$= KQ \exp(\mu^2 Dt)\{1 - \operatorname{erf}[\mu\sqrt{(Dt)}]\}$$

L'activité avant tout traitement de diffusion est:

$$A_0 = K \,.\, Q$$

d'où:

$$A/A_0 = \exp(\mu^2 Dt)\{1 - \operatorname{erf}[\mu\sqrt{(Dt)}]\} \quad (4.1.1)$$

Il est commode de tracer une courbe d'étalonnage donnant le rapport A/A_0 en fonction de $\mu^2 Dt$ (Fig. 5).

La méthode implique que la loi d'absorption soit effectivement exponentielle. Jaumot et Smith[3] ont pu l'appliquer au cas où l'isotope (en l'espèce Zn^{65}) émet un rayonnement complexe. Il est dans ce cas possible de mettre le facteur d'absorption sous la forme d'une somme d'exponentielles.

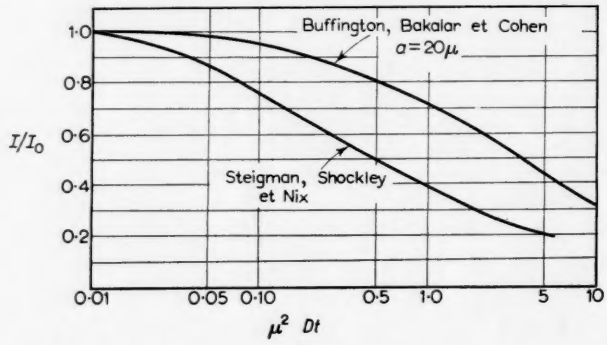

Fig. 5.

Pour améliorer les conditions de la diffusion, Buffington *et al.*[11] ont choisi de faire diffuser un dépôt épais au lieu d'une couche infiniment mince. Ils ont étudié de cette manière l'autodiffusion du fer en utilisant l'isotope Fe^{55} (émetteur de rayonnements de capture K); les échantillons étaient recouverts d'une couche de fer radioactif de 20 μ d'épaisseur. La solution du problème est alors donnée par l'équation (1.1.4). On montre alors que:

$$\frac{A}{A_0} = \frac{\exp(\mu^2 Dt)}{2[1 - \exp(-\mu a)]} \left\{\exp(\mu a) \times \left[1 - \operatorname{erf}\left(\frac{a + 2\mu Dt}{2\sqrt{(Dt)}}\right)\right] - \exp(-\mu a) \times \left[1 - \operatorname{erf}\left(\frac{-a + 2\mu Dt}{2\sqrt{(Dt)}}\right)\right]\right\} + \frac{\operatorname{erf} a/2\sqrt{(Dt)}}{1 - \exp(-\mu a)},$$

a étant l'épaisseur du dépôt. Il est encore

possible de tracer une courbe $A/A_0 = f(\mu^2 Dt)$. Nous la reproduisons sur la Fig. 5 dans le cas où $a = 20\ \mu$. La situation relative des deux courbes montre que la méthode de Buffington *et al.* est un peu moins sensible que la méthode de Steigman *et al.* Elle présente par contre certains avantages de sécurité: par exemple, une légère oxydation du dépôt n'a pas d'importance, puisque ce sont surtout les atomes radioactifs proches de l'interface dépôt–métal qui contribuent à la diffusion.

L'aspect des courbes précédentes permet de fixer les limites de la méthode. On peut admettre que la limite se place vers $A/A_0 \sim 0{,}9$. Alors $\mu^2 Dt \sim 0{,}1$. Dans le cas d'un rayonnement fortement absorbé (exemple: Fe^{55}–$\mu = 700\ cm^{-1}$), après un recuit de 10 jours, il est possible de mesurer un coefficient de diffusion de l'ordre de $2 \cdot 10^{-13}$. On peut d'ailleurs mesurer des coefficients plus faibles, si l'absorption est plus importante. La méthode n'offre par contre qu'un intérêt limité si les rayonnements sont très peu absorbés (exemple: Co^{60}; $\mu = 0{,}3\ cm^{-1}$).

Buffington *et al.*[11] ont tenté de chiffrer les erreurs qui s'introduisent dans la méthode de décroissance superficielle. L'erreur sur la connaissance de A/A_0 est fixée à 2 pour cent, l'erreur sur a à 1 pour cent et celle sur μ à 2 pour cent. Au total, l'erreur sur la détermination de chaque coefficient de diffusion est de l'ordre de 10 pour cent. Il semble que, dans le cas général, l'erreur sur μ puisse être estimée à plus de 2 pour cent. Si μ est mesuré par variation de l'activité après interposition entre la source et le compteur de feuilles métalliques, on a une précision d'autant plus grande que μ est plus petit.

3.2.2. La méthode de Gruzin. La méthode de décroissance superficielle n'est pas applicable, comme nous l'avons vu, au cas où les rayonnements sont trop peu absorbés. Gruzin[12] a été ainsi conduit à imaginer une méthode combinant la méthode de sectionnement et les méthodes d'absorption.

Soit un échantillon métallique dans lequel s'est effectuée une diffusion à partir d'une couche mince. Comme nous l'avons vu, la concentration à la distance x est:

$$c = \frac{Q}{\sqrt{(\pi Dt)}} \exp\,(-x^2/4Dt)$$

Abrasons l'échantillon jusqu'à la distance x_n de l'interface de départ et mesurons son activité totale restante. La valeur obtenue est:

$$I_n = K \int_{x_n}^{\infty} \frac{Q}{(\sqrt{\pi Dt})} \exp\,(-x^2/4Dt) \times \exp\,[-\mu(x - x_n)]\,dx$$

K étant un facteur de comptage. Le facteur $\exp\,[-\mu(x - x_n)]$ tient compte du fait que la surface $x = x_n$ est maintenant une surface libre. On a, en faisant le changement de variable:

$$\xi = \frac{x}{2\sqrt{(Dt)}} + \mu\sqrt{(Dt)}\,;\ I_n = k \exp\,(\mu^2 Dt + \mu x_n)\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{[x_n/2\sqrt{(Dt)}] + \mu\sqrt{(Dt)}} \exp\,(-\xi^2)\,d\xi\right]$$

en posant $\qquad k = K \,.\, Q$

On en déduit facilement que:

$$\mu I_n - \frac{\partial I_n}{\partial x_n} = \frac{k}{\sqrt{(\pi Dt)}} \exp\,[-x_n{}^2/4Dt]$$

Cette formule montre que la méthode est intéressante dans deux cas limites:

3.2.2.1. Cas d'un rayonnement peu absorbé (exemple: Co^{60}–émetteur γ; $\mu = 0{,}3\ cm^{-1}$) Gruzin.[12]

Comme:

$$\mu I_n \ll \frac{\partial I_n}{\partial x},$$

on a:

$$\mathrm{Log}\,\frac{\partial I_n}{\partial x_n} = A - \frac{x_n{}^2}{4Dt},$$

d'où le coefficient de diffusion.

3.2.2.2. Cas d'un rayonnement très absorbé (exemple: Ni^{63}–émetteur β de très faible énergie)–Hoffman *et al.*[13]

Comme:

$$\frac{\partial I_n}{\partial x_n} \ll \mu I_n,$$

on a:

$$\text{Log } I_n = B - \frac{x_n^2}{4Dt}$$

La méthode de Gruzin n'est applicable en toute rigueur que si l'absorption des rayonnements est effectivement exponentielle. Dans le cas où l'on étudie des radioéléments émetteurs de rayonnements β, il y a donc lieu de vérifier au préalable si cette hypothèse est acceptable (voir 2.1).

SEIBEL[14] a pu montrer récemment que la relation de Gruzin était plus générale. Supposons en effet que la concentration à la distance x soit donnée par une fonction quelconque $c(x)$. Si nous utilisons les mêmes notations que précédemment, on a:

$$I_n = K \int_{x_n}^{\infty} c(x) \exp [-\mu(x - x_n)]\, dx$$

On en tire que:

$$\mu I_n = \mu K \int_{x_n}^{\infty} c(x) \exp [-\mu(x - x_n)]\, dx$$

et:

$$\frac{\partial I_n}{\partial x} = \mu K \exp (\mu x_n) \int_{x_n}^{\infty} c(x) \exp (-\mu x)\, dx + K \exp (\mu x_n) \exp (-\mu x_n) c x_n$$

d'où:

$$\mu I_n - \frac{\partial I_n}{\partial x_n} = K c(x_n)$$

Cette remarque doit permettre une notable extension de la méthode de Gruzin.

Le principal intérêt de la méthode de Gruzin est qu'il n'est plus utile de récupérer et de traiter les copeaux résultant de chaque abrasion. Les précautions expérimentales sont les mêmes que pour la méthode classique de sectionnement (voir 3.1.3).

3.2.3. La méthode de Zhoukhovitzky et Geodakyan. La méthode de ZHOUKHOVITZKY et GEODAKYAN[15] utilise un échantillon "*épais*" (épaisseur supérieure à la profondeur de pénétration) à la surface duquel est déposée une couche très mince des isotopes. Si nous représentons le facteur d'absorption par la fonction inconnue $f(x)$, on a, en utilisant les mêmes notations que précédemment:

$$\frac{A}{A_0} = \frac{1}{\sqrt{(\pi Dt)}} \int_0^{\infty} \exp (-x^2/4Dt) f(x)\, dx$$

Supposons que t soit très grand. Il est alors possible de développer $\exp (-x^2/4Dt)$ en série. On obtient:

$$\exp (-x^2/4Dt) = 1 - \frac{x^2}{4Dt} + \frac{x^4}{32D^2t^2} \cdots,$$

d'où:

$$\frac{A}{A_0} = \frac{1}{\sqrt{(\pi Dt)}} \left[\int_0^{\infty} f(x)\, dx - \int_0^{\infty} \frac{x^2}{4Dt} f(x)\, dx + \ldots \right]$$

Si l'on peut se limiter au premier terme:

$$\frac{A}{A_0} = \frac{1}{\sqrt{(\pi Dt)}} \int_0^{\infty} f(x)\, dx$$

La courbe $A/A_0 = f(1/\sqrt{t})$ a donc pour pente:

$$m = 1/\sqrt{(\pi D)} \int_0^{\infty} f(x)\, dx$$

Pour déterminer $\int_0^{\infty} f(x)\, dx$, on effectue un dépôt infiniment mince à la surface d'un échantillon très épais. On mesure son activité, soit I_0. On fond ensuite le métal et on le coule de manière à ce qu'il reprenne la même forme que dans la première expérience. On mesure à nouveau son activité, soit I_∞. Après la fusion, le radioélément est *uniformément réparti* dans la masse métallique. Si δ est l'épaisseur de l'échantillon, la concentration moyenne par unité de longueur est:

$$I_0/\delta$$

Or

$$I_\infty = \int_0^{\infty} \frac{I_0}{\delta} f(x)\, dx$$

Donc,

$$\int_0^{\infty} f(x)\, dx = \frac{I_\infty}{I_0} \delta$$

On en déduit que:

$$m = \frac{1}{\sqrt{(\pi D)}} \frac{I_\infty}{I_0} \delta$$

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d'où:

$$D = \frac{I_\infty^2}{I_0^2}\frac{\delta^2}{m^2\pi}.$$

La connaissance de $f(x)$ est ainsi éliminée.

Il est nécessaire d'attendre un temps suffisant pour qu'on puisse se limiter au premier terme du développement (exemple: 5 hr pour l'argent à 850°C); le temps est évidemment d'autant plus grand que la température de recuit est plus élevée: si les rayonnements ont une trop grande énergie, l'absorption est faible, le temps de recuit peut devenir prohibitif. On a alors intérêt à utiliser des filtres, de manière à ne conserver pratiquement que les rayonnements les plus absorbés. La détermination de la quantité I_∞ peut d'autre part présenter des difficultés dans l'homogénéisation de l'isotope radioactif. Jusqu'à présent, la méthode a été peu appliquée. Ses promoteurs l'ont utilisée pour étudier l'autodiffusion de l'argent.

3.2.4. La méthode de Kryukov et Zhoukhovitzky. La méthode précédente ne nécessite pas la connaissance directe du facteur d'absorption, mais oblige à déterminer la grandeur I_∞, ce qui peut être difficile. KRYUKOV et ZHOUKHOVITZKY[16] ont donc mis au point une autre technique qui ne nécessite pas la connaissance du facteur d'absorption.

Si l'on effectue la diffusion d'une couche très mince de radioisotope dans une plaquette mince, la concentration dans la plaquette est donnée, au bout d'un certain temps, par l'équation (1.2.3):

$$c(x) = c_0\frac{h}{l}\left[1 + 2\cos\frac{\pi x}{l}\exp\left(-\pi^2 Dt/l^2\right)\right]$$

Mesurons l'activité de la plaquette, I_1, en plaçant face au compteur la face qui a reçu le dépôt. On a:

$$I_1 = K\int_0^l c(x)f(x)\,dx$$

K étant le facteur de comptage et $f(x)$, le facteur d'absorption des rayonnements.

Retournons la plaquette et mesurons l'activité I_2. On a:

$$I_2 = K\int_0^l c(x)f(l-x)\,dx$$

En reportant la valeur de $c(x)$, on trouve:

$$I_1 = K\int_0^l c_0\frac{h}{l}[1 + 2\cos(\pi x/l) \times \exp(-\pi^2 Dt/l^2)]f(x)\,dx$$

et:

$$I_2 = K\int_0^l c_0\frac{h}{l}[1 + 2\cos(\pi x/l) \times \exp(-\pi^2 Dt/l^2)]f(l-x)\,dx$$

On a donc

$$\frac{I_1}{I_2} = \frac{\int_0^l [1 + 2\cos(\pi x/l)\exp(-\pi^2 Dt/l^2)] \times f(x)\,dx}{\int_0^l [1 + 2\cos(\pi x/l)\exp(-\pi^2 Dt/l^2)] \times f(l-x)\,dx}$$

Or:

$$\int_0^l f(x)\,dx = \int_0^l f(l-x)\,dx$$

Donc:

$$\frac{I_1}{I_2} = \frac{\int_0^l f(x)\,dx + 2\int_0^l \cos(\pi x/l)\exp(-\pi^2 Dt/l^2)f(x)\,dx}{\int_0^l f(x)\,dx + 2\int_0^l \cos[\pi(l-x)]\exp(-\pi^2 Dt/l^2)f(x)\,dx}$$

Posons

$$k = \frac{2\int_0^l \cos(\pi x/l)f(x)\,dx}{\int_0^l f(x)\,dx}$$

On a:

$$\frac{I_1}{I_2} = \frac{1 + k\exp(-\pi^2 Dt/l^2)}{1 - k\exp(-\pi^2 Dt/l^2)}$$

On en tire que

$$\mathrm{Log}\frac{I_1 - I_2}{I_1 + I_2} = \log k - \frac{\pi^2 D}{l^2}t,$$

relation simple qui ne fait pas intervenir la connaissance de $f(x)$. La méthode est sans doute une des plus intéressantes parmi les techniques d'étude de l'autodiffusion. Son seul inconvénient est la préparation d'échantillons très minces (100 μ au maximum), ce qui n'est pas toujours possible surtout si l'on étudie l'autodiffusion dans des monocristaux.[17] Elle permet par contre la mesure de faibles coefficients de diffusion

en quelques jours (par exemple, la manipulation dure environ 10 jours pour la mesure, à l'aide d'un échantillon de 70 μ d'épaisseur, d'un coefficient de diffusion égal à 10^{-12}). La relation linéaire commence, dans les mêmes condition, à être vérifiée au bout de 3 jours. L'emploi de la méthode commence à se répandre (autodiffusion de l'argent, du nickel dans les alliages Fe–Ni, du fer α).

3.3. La méthode autoradiographique

Jusqu'à présent, nous n'avons envisagé la détection des rayonnements que par leur action ionisante dans un compteur de Geiger. Mais il est également possible d'utiliser leur action sur les émulsions photographiques. Comme nous l'avons signalé, les rayons γ sont beaucoup moins actifs sur les sels d'argent que les rayons β. C'est pourquoi la méthode autoradiographique s'adresse surtout à ces derniers.

Le principe de la mesure des coefficients de diffusion par la technique autoradiographique consiste à déterminer le noircissement d'une émulsion en fonction de la distance de la couche métallique envisagée à l'interface de dépôt. Le noircissement est proportionnel à la concentration en atomes radioactifs, dans la mesure où la loi de réciprocité est vérifiée. On sait que cette loi cesse d'être valable si l'exposition est trop grande. On n'a donc pas avantage à effectuer des dépôts trop actifs.

De manière à éviter d'avoir à découper des tranches successives dans l'échantillon, on utilise la méthode de la coupe biaise. Après le traitement de diffusion, on usine une section faisant l'angle α avec le dépôt.

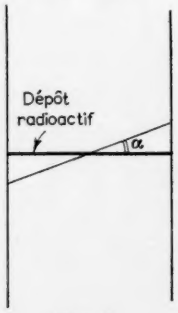

FIG. 6.

On applique la face ainsi mise à nu sur une émulsion, puis on mesure, à l'aide d'un microphotomètre, la noircissement le long de la coupe biaise.

Pour définir avec précision la position de l'interface de départ, on a intérêt à effectuer la diffusion dans un milieu infini, en soudant au métal recouvert de son dépôt un cylindre de même diamètre du métal inactif (Fig. 6). De cette manière, la courbe de noircissement est symétrique.

Il faut noter que la pellicule est impressionnée, non seulement par les rayonnements issus d'atomes localisés à la surface, mais également par les rayonnements incomplètement absorbés provenant de couches plus éloignées. Les résultats doivent donc être corrigés de la manière suivante due à KURTZ *et al.*[18]

Supposons que l'absorption obéisse à une loi exponentielle. Considérons (Fig. 7) une bande active située à la distance y

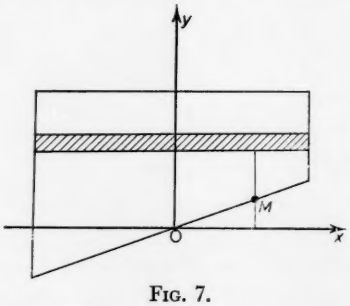

FIG. 7.

de l'interface de départ. La concentration $c(y)$ est égale a:

$$c(y) = \frac{Q}{2\sqrt{(\pi Dt)}} \exp(-y^2/4Dt)$$

puisque la diffusion a lieu dans un milieu infini. La contribution au noircissement au point M distant de x tg α de l'interface de départ est donc:

$$I(x) = \int_{x \operatorname{tg}\alpha}^{\infty} c(y) \exp[-\mu(y - x \operatorname{tg}\alpha)]\, dy$$

On a donc:

$$\frac{I(x)}{I_0} = \frac{\exp[\mu x \operatorname{tg}\alpha]}{2\sqrt{(\pi Dt)}} \times \int_{x \operatorname{tg}\alpha}^{\infty} \exp\left[-\frac{y^2}{4Dt} - \mu y\right] dy$$

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Posons

$$\xi = \frac{y}{2\sqrt{(Dt)}} + \mu\sqrt{(Dt)}$$

On a:

$$\frac{I_l}{I_0} = \frac{\exp\left[\mu x \operatorname{tg}\alpha + \mu^2 Dt\right]}{\sqrt{\pi}} \times \left[\int_0^{\infty} \exp\left(-\xi^2\right) d\xi - \int_0^{\xi_0} \exp\left(-\xi^2\right) d\xi\right]$$

où:

$$\xi_0 = \frac{x \operatorname{tg}\alpha}{2\sqrt{(Dt)}} + \mu\sqrt{(Dt)}$$

On peut exprimer I_l/I_0 sous la forme

$$\frac{I_l}{I_0} = \frac{\exp\left[-\mu x \operatorname{tg}\alpha + \mu^2 Dt\right]}{2} \left[1 - \operatorname{erf}\xi_0\right]$$

Si ξ_0 est grand:

$$\frac{I_l}{I_0} = \frac{\exp\left[-x^2 \operatorname{tg}^2\alpha/4Dt\right]}{2\sqrt{\pi}} \left[\frac{1}{\xi_0} - \frac{1}{2\xi_0^3} + \frac{3}{4\xi_0^5} \cdots\right]$$

Si nous ne conservons que le premier terme du développement:

$$\frac{I_l}{I_0} = \frac{\exp\left(-x^2 \operatorname{tg}^2\alpha/4Dt\right)}{2\xi_0\sqrt{\pi}}$$

On en tire

$$\operatorname{Log}\frac{I_l}{I_0} = -\frac{x^2 \operatorname{tg}^2\alpha}{4Dt} - \operatorname{Log}\xi_0 + c^{te}$$

Or:

$$\xi_0 = \frac{x \operatorname{tg}\alpha}{2\sqrt{(Dt)}} + \mu\sqrt{(Dt)} = \mu\sqrt{(Dt)}\left[1 + \frac{x \operatorname{tg}\alpha}{2\mu Dt}\right]$$

Donc:

$$\log\frac{I_l}{I_0} = c^{te} - \frac{x^2 \operatorname{tg}^2\alpha}{4Dt} - \log\left[1 + \frac{x \operatorname{tg}\alpha}{2\mu Dt}\right]$$

et:

$$\frac{d\log\dfrac{I_l}{I_0}}{d(x^2 \operatorname{tg}^2\alpha)} = -\frac{1}{4Dt}\left(1 + \frac{1}{\mu x \operatorname{tg}\alpha}\right), \quad \text{si } \frac{x \operatorname{tg}\alpha}{2\mu Dt} \ll 1$$

Le facteur correctif $-\dfrac{1}{4Dt\ \mu x \operatorname{tg}\alpha}$ est négligeable si $\mu x \operatorname{tg}\alpha$ est suffisamment grand. Cela signifie que la méthode ne nécessite pas la connaissance de μ si l'absorption est très forte dans le métal. La méthode a été utilisée pour l'étude de l'autodiffusion de l'or et de la diffusion de l'or dans les alliages Au–Ni. Au^{198} émet un rayonnement très complexe, mais contenant 99 pour cent de β, d'énergie maximum 0,96 MeV. Cette valeur n'étant pas très élevée, la correction n'intervient pratiquement pas pour $x^2 \operatorname{tg}^2\alpha > 20 \cdot 10^{-6}$ cm² (alliage Au–80 % Ni). Si $\alpha = 3°$, la méthode est donc directement applicable pour $x > 1$ mm.

4. LES MÉTHODES D'ÉTUDE DE L'AUTODIFFUSION INTERGRANULAIRE ET SUPERFICIELLE

4.1. Existence de la diffusion intergranulaire

Nous avons jusqu'à présent traité uniquement le cas de la diffusion en volume, c'est à dire celui d'une avance uniforme du front de diffusion sur toute la largeur de l'éprouvette. Dans ces conditions, la résolution des équations de la diffusion est assez simple. Il ne faut cependant pas oublier que l'autodiffusion est un moyen d'étude très précieux de la structure atomique des métaux et qu'à ce titre, elle doit faire intervenir les caractéristiques propres aux milieux polycristallins. Cet aspect, fondamental en physique des métaux, est aussi très complexe et nous nous limiterons au rappel de quelques notions indispensables pour comprendre les méthodes expérimentales actuellement utilisées.

Un métal est formé d'un agrégat de cristaux ou de grains d'orientation cristallographique différente séparés les uns des autres par les contours ou les joints de grains que révèle l'attaque par des réactifs chimiques convenables. Dans le cas général, les

grains sont des cristaux presque parfaits alors que la structure des joints de grains est nécessairement imparfaite. Les joints constituent en effet une région de raccordement entre deux cristaux contigus d'orientation différente dont la largeur est d'autant plus grande que la désorientation est plus importante. L'hypothèse ancienne du joint de grains constitué par du métal amorphe a été abandonnée au profit de cette théorie du *réseau de transition*, qui est plus conforme à la variation des propriétés chimiques, physiques ou mécaniques des contours de grains en fonction de la désorientation des cristaux contigus.[19]

En première approximation, on peut dire que la structure des joints de grains est d'autant plus imparfaite que la désorientation entre cristaux voisins est plus grande. Si la désorientation est nulle, le raccordement se fait d'une manière parfaite ainsi que dans le cas où les cristaux sont en position relative de macle. Mais ces cas de raccordement parfait sont rares. Le plus souvent, les cristaux se raccordent d'une manière imparfaite de sorte que la structure du joint de grains peut être grossièrement représentée par un ensemble d'imperfections telles que lacunes et dislocations. C'est seulement dans le cas d'une désorientation très faible (inférieure à quelques degrés) que la structure du joint peut être décrite géométriquement d'une manière simple par une succession de dislocations. Les conséquences de cette structure des joints, plus ou moins perturbée en comparaison de celle de la masse des cristaux, sont de favoriser l'autodiffusion d'un élément radioactif d'autant plus que la désorientation entre grains voisins est plus importante. L'expérience justifie ces prévisions, en fournissant un argument au mécanisme de l'autodiffusion: le déplacement des atomes diffusants aurait lieu par échange de position entre les atomes métalliques et les lacunes du réseau.

D'un point de vue formel, il est difficile de traiter le cas d'un joint de grains réel. C'est pourquoi les seules théories existantes considèrent le joint comme un *milieu continu* à l'échelle macroscopique dans lequel on peut appliquer les lois classiques de la diffusion. Le coefficient de diffusion aux joints de grains est alors $D_j \neq D_v$, coefficient de diffusion dans le volume des cristaux. L'assimilation d'un joint intergranulaire à un milieu continu ne se justifie que si le joint sépare des cristaux *fortement désorientés*. Les théories que nous allons examiner ne sont donc applicables expérimentalement que si l'on étudie des métaux à très fine granulation. De cette manière, la probabilité d'avoir des joints de très forte désorientation est grande, ce qui permet de donner aux théories un aspect statistique, le seul abordable dans les expériences sur métaux polycristallins.

4.2. Les théories de Fisher et Whipple sur l'autodiffusion intergranulaire

Considérons un joint de largeur δ et dans lequel le coefficient de diffusion est égal à D_j séparant deux cristaux dans lesquels le

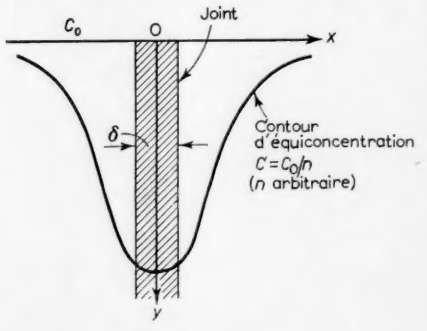

FIG. 8.

coefficient de diffusion est égal à D_v (Fig. 8) ($D_j \gg D_v$). Les atomes de substance diffusante situés à l'aplomb du joint y pénètrent très facilement et subissent ensuite une diffusion latérale dans le volume des cristaux contigus.

Pour simplifier, nous supposerons que le joint est normal à la surface libre du bicristal et que la concentration de substance diffusante est maintenue constante et égale à c_0 à la surface du métal. Nous rapporterons les coordonnées à l'axe Ox parallèle à la surface libre et à l'axe Oy, axe du joint de grains.

Dans le volume des cristaux, la diffusion est régie par la loi de Fick que l'on peut

écrire, sous sa forme la plus générale:

$$D_v \Delta c_v = \frac{\partial c_v}{\partial t} \qquad (4.2.1)$$

et, pour le joint:

$$D_j \Delta c_j = \frac{\partial c_j}{\partial t} \qquad (4.2.2)$$

c_v et c_j représentant les concentrations dans le volume des cristaux et dans le joint intergranulaire, respectivement.

Au point d' intersection de la limite du joint et d'une courbe arbitraire d'équiconcentration:

(a) la concentration est la même dans le joint et dans la masse. Donc:

$$(c_j)_{x=\pm(\delta/2)} = (c_v)_{x=\pm(\delta/2)} \qquad (4.2.3.)$$

(b) la courbe d'équiconcentration est continue. Donc:

$$D_v \left(\frac{\partial c_v}{\partial x}\right)_{x=\pm(\delta/2)} = D_j \left(\frac{\partial c_j}{\partial x}\right)_{x=\pm(\delta/2)} \qquad (4.2.4)$$

FISHER[20] a traité le problème dans l'approximation suivante: la courbe d'équiconcentration est évidemment symétrique par rapport à l'axe Oy. On a donc:

$$c_j(x, y, t) = c_j(0, y, t) + \frac{x^2}{2}\left[\frac{\partial^2 c_j(x, y, t)}{\partial x^2}\right]_{x=0} + \cdots$$

Reportons dans (6.2.2). On trouve que:

$$D_j\left[\frac{\partial^2 c_j(0, y, t)}{\partial y^2} + \left(\frac{\partial^2 c_j}{\partial x^2}\right)_{x=0}\right] = \frac{\partial c_j(0, y, t)}{\partial t} \qquad (4.2.5)$$

Si nous négligeons les termes en δ^2, les équations aux limites (4.2.3) et (4.2.4) deviennent, au voisinage du joint:

$$\begin{cases} c_v\left(\frac{\delta}{2}, y, t\right) = c_j(0, y, t) \\ D_v\left(\frac{\partial c_v}{\partial x}\right)_{x=(\delta/2)} = D_j \frac{\delta}{2}\left(\frac{\partial^2 c_j}{\partial x^2}\right)_{x=0} \end{cases} \qquad (4.2.6)$$

Eliminons $c_j(0, y, t)$ et $\left[\frac{\partial^2 c_j(x, y, t)}{\partial x^2}\right]_{x=0}$ entre (4.2.5) et (4.2.6); on trouve alors que:

$$D_j \frac{\partial^2 c_v}{\partial y^2} + 2\frac{D_v}{\delta}\frac{\partial c_v}{\partial x} = \frac{\partial c_v}{\partial t} \qquad (6.2.7)$$

donne la valeur de la concentration à la limite du joint intergranulaire, c'est-à-dire pour $x = \pm\frac{\delta}{2}$:

FISHER a montré que la solution de cette équation pouvait être représentée par:

$$c_v = c_0 \exp\left[-\frac{1}{\pi^{1/4}}\frac{\eta}{\beta^{1/2}}\right] \operatorname{erfc}\frac{\xi}{2} \qquad (4.2.8)$$

dans laquelle:

$$\xi = \frac{x - (\delta/2)}{\sqrt{(D_v t)}};\ \eta = \frac{y}{\sqrt{(D_v t)}};\ \beta = \frac{D_j \delta}{2 D_v^{3/2} t^{1/2}}$$

Au contraire, WHIPPLE[21] est parvenu à donner une solution rigoureuse au problème. Il a montré que:

$$\frac{c_v}{c_0} = \operatorname{erfc}\eta + \frac{\eta}{\sqrt{\pi}}\int_0^\infty \exp\left(-\frac{\eta^2\tau^2}{4}\right) \times \operatorname{erfc}\frac{1}{2}\left(\frac{1}{\tau^2\beta} - \frac{1}{\beta} + \xi\right) d\tau \qquad (4.2.9)$$

Si ξ est petit, c'est-à-dire si l'on se trouve près du joint et si $\eta \gg 1$, c'est-à-dire si l'on étudie la diffusion à grande profondeur, on peut utiliser la formule:

$$\frac{c_v}{c_0} = 1{,}159\ \beta^{1/3}\ \eta^{-2/3} \exp\left[-0{,}473\ \beta^{-2/3}\ \eta^{4/3} - 0{,}396\ \beta^{-4/3}\ \eta^{2/3}\ (1 - \beta\xi)\right] \qquad (4.2.10)$$

En réalité, cette formule n'a de sens que si l'on étudie des concentrations déjà *très faibles*. Le calcul montre que c_v/c_0 doit être $<0{,}1$ pour qu'on puisse l'utiliser.

Formellement, les équations (4.2.8) et (4.2.10) sont très différentes. Considérons cependant la concentration très près du joint ($\xi \sim 0$); WHIPPLE a déterminé par le calcul la forme des contours d'équiconcentration pour les trois valeurs $\beta = 0{,}1$, $\beta = 1{,}0$ et $\beta = 10{,}0$. On connaît alors, pour une valeur c/c_0 fixée, la profondeur de pénétration dans un joint caractérisée par la variable réduite η. On peut donc, en appliquant l'équation (6.2.8) utiliser la théorie de FISHER et calculer quelle est,

dans cette hypothèse, la concentration dans le joint à la profondeur réduite.

On peut ainsi dresser les tableaux suivant:

TABLEAU 1a. $\beta = 0{,}1$

η	c/c_0 Whipple	c/c_0 Fisher
0,36	0,80	0,42
0,76	0,60	0,16
1,24	0,40	0,05
1,91	0,20	10^{-5}

TABLEAU 1b. $\beta = 1{,}0$

η	c/c_0 Whipple	c/c_0 Fisher
0,50	0,80	0,69
1,00	0,60	0,48
1,66	0,40	0,29
2,56	0,20	0,14

TABLEAU 1c. $\beta = 10{,}0$

η	c/c_0 Whipple	c/c_0 Fisher
1,00	0,80	0,79
2,12	0,60	0,60
3,62	0,40	0,42
5,87	0,20	0,25

L'examen de ces valeurs montre que, si β n'est pas trop petit, l'accord entre les deux expressions est bon (résultat d'ailleurs vérifié expérimentalement par YUKAWA et SINNOTT.[22] L'accord est d'autant meilleur que β est plus grand. Que représente cette condition, dans le cas concret de l'autodiffusion intergranulaire des métaux?

On a:

$$\beta = \frac{\delta}{2\sqrt{(D_v t)}} \frac{D_j}{D_v}.$$

Si nous supposons que l'approximation de FISHER est valable pour $\beta > 10$, on a:

$$D_j/D_v > 20\sqrt{(D_v t)}/\delta$$

δ, largeur du joint, est peu connue. Nous la supposerons égale à 10 Å soit 10^{-7} cm. Nous supposerons également que le temps de recuit ne dépasse pas quelques jours, par exemple que $t = 64 \cdot 10^4$ sec. L'hypothèse de FISHER est alors vérifiée si:

$$D_j/D_v > 16 \cdot 10^{-10}\sqrt{D_v}.$$

Ainsi, si $D_v \sim 10^{-14}$, on voit que D_j doit être $> 1{,}6 \cdot 10^{-12}$. Ce résultat est parfaitement en accord avec les observations expérimentales. Ainsi, HOFFMAN et TURNBULL[23] en étudiant l'autodiffusion de l'argent, ont montré qu'à basse température, où

$$D_v \sim 10^{-14}, \quad D_j \sim 10^{-7}.$$

A mesure que croît la température, le rapport minimum pour qu'on puisse appliquer la théorie de FISHER doit augmenter. Or, ce rapport diminue avec l'augmentation de température, ce qui signifie que la diffusion intergranulaire devient de moins en moins prépondérante. On trouve ainsi un résultat que viennent confirmer les déterminations expérimentales: *la théorie de Fisher ne peut s'utiliser qu'à basse température, dans un domaine où la diffusion intergranulaire est très importante devant la diffusion en volume.*

Le formalisme des équations de FISHER et WHIPPLE amène à faire un certain nombre de remarques:

(1) la largeur du joint est supposée constante. Cette hypothèse n'a aucun support expérimental: d'une part, la largeur, définie géométriquement, peut varier d'un point à l'autre le long d'un joint séparant deux cristaux désorientés d'une manière quelconque; d'autre part, sous l'action de l'agitation thermique, elle peut varier avec la température. Aux deux extrêmes, un joint de macle n'a pas d'épaisseur et un joint de forte désorientation est tellement perturbé que probablement sa largeur est de l'ordre de plusieurs distances interatomiques. Signalons que TURNBULL et HOFFMAN[24] ont essayé de revoir le problème de la diffusion intergranulaire dans le cas d'un joint assimilable à un ensemble de dislocations isolées. Il faut espérer un développement de ces théories qui, dans certains cas simples, tiennent compte de la structure discontinue réelle des joints de grains.

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(2) la théorie suppose que le joint est normal à la surface, ce qui est loin d'être toujours le cas (voir plus bas).

(3) on admet que la concentration en substance diffusante à la surface du dépôt reste constante. Dans la pratique, il en va différemment, car le plus souvent, on effectue les expériences en déposant une *mince* couche radioactive à la surface du métal. Cependant, la condition $c_0 = c^{te}$ est souvent approchée. A basse température, la diffusion s'effectue facilement dans les joints et très difficilement dans la masse des cristaux. Si le recuit de diffusion n'est pas trop long, la quantité de substance transportée dans les joints est faible et la concentration c varie peu. Le nombre d'expériences réalisées en admettant les hypothèses de FISHER montre d'ailleurs que ce facteur n'a que peu d'importance *à basse température*.

(4) il est rare que, dans la pratique, on étudie le comportement d'un joint unique. On utilise au contraire des échantillons polycristallins. Les restrictions que nous venons d'énoncer s'atténuent alors nettement. Si le nombre de grains dans l'éprouvette est important, on pourra supposer statistiquement que les joints sont identiques et normaux à la surface. Dans ces conditions, il devient possible de définir un coefficient de diffusion aux joints, D_j, et une énergie d'activation Q_j, moyens. Ces valeurs risquent de n'avoir qu'une signification théorique restreinte, par leur nature statistique même, mais présentent un gros intérêt dans la pratique, où certains phénomènes sont liés à la diffusion intergranulaire (frittage par exemple). La grosseur des grains ne doit cependant pas être trop petite. En effet, les théories de FISHER et WHIPPLE n'envisagent pas les interactions possibles entre différents joints rapprochés. Si les joints se rapprochent trop, les contours d'équiconcentration se recouvrent et il n'est plus possible d'envisager le comportement d'un ensemble de joints comme la simple addition du comportement d'un joint unique. Nous avons personnellement effectué un certain nombre d'expériences sur l'autodiffusion intergranulaire du fer cubique centré. Nous avons ainsi pu constater que la théorie de FISHER était applicable à basse température sur des échantillons polycristallins. Par exemple, à 650°C, on ne décèle plus de diffusion intergranulaire à l'aide d'un compteur de Geiger au-delà d'une profondeur d'environ 40 μ. Comme nous avons opéré sur des échantillons d'environ 0,5 cm² de surface dans lesquels la grosseur moyenne du grain était de l'ordre de 100 μ, la méthode présente alors toute sa valeur.

4.3. Réalisations expérimentales

La plupart des techniques utilisées font appel aux procédés de comptage et à l'application de la théorie de FISHER. Nous avons vu (4.2.8) que la concentration C_v est donnée par:

$$c_v = c_0 \exp\left[-\frac{1}{\pi^{1/4}}\frac{\eta}{\beta^{1/2}}\right] \operatorname{erfc}\left(\frac{x}{2\sqrt{(D_v t)}}\right).$$

si l'on néglige la largeur du joint.

Considérons un joint unique. Supposons qu'on découpe, à la profondeur y, une tranche d'épaisseur y. A un facteur de comptage k près, l'intensité de rayonnement localisée dans la couche y est:

$$I_y = k \int_y^{y+\Delta y} \int_{-\infty}^{+\infty} \exp\left[-\frac{1}{\pi^{1/4}}\frac{y}{\sqrt{(D_v t)}}\frac{1}{\beta^{1/2}}\right] \times \operatorname{erfc}\frac{x}{2\sqrt{(D_v t)}}\, dx\, dy$$

soit

$$I_y = k' \exp\left[-\frac{1}{\pi^{1/4}}\cdot\frac{1}{\sqrt{(D_v t)}}\frac{1}{\beta^{1/2}}y\right]\Delta y,$$

k' étant une nouvelle constante résultant de l'intégration

$$\int_{-\infty}^{+\infty} \operatorname{erfc}\frac{x}{2\sqrt{(D_v t)}}\, dx$$

L'activité spécifique $\frac{I_y}{\Delta y}$ est donc

$$A_y = k' \exp\left[-\frac{1}{\pi^{1/4}}\frac{1}{\sqrt{(D_v t)}}\frac{1}{\beta^{1/2}}y\right]$$

Il en résulte que:

$$\operatorname{Log} A_y = k'' - \frac{1}{\pi^{1/4}}\cdot\frac{1}{\sqrt{(D_v t)}}\cdot\frac{1}{\beta^{1/2}}y$$

La quantité log A_y varie donc linéairement avec y. La pente de la droite est:

$$m = -\frac{2^{1/2}}{(\pi D_v t)^{1/4}} \sqrt{\left(\frac{D_v}{D_j \delta}\right)},$$

d'où D_j connaissant D_v:

La technique a été largement utilisée. Ses modalités d'application sont les mêmes que pour la méthode classique de sectionnement (voir plus haut).

La méthode autoradiographique a été utilisée par YUKAWA et SINNOTT[22] dans le cas de la diffusion du nickel radioactif dans le cuivre, puis par UPTHEGROVE et SINNOTT[25] dans le cas de l'autodiffusion du nickel. Ces auteurs ont tenté de plus d'aborder la partie structurale du problème en tirant profit des techniques autoradiographiques modernes (emploi des émulsion détachables, ou "stripping films") permettant un grandissement de l'ordre de 500. Ils ont pu de cette manière abandonner l'approximation statistique qui est celle des méthodes de sectionnement et étudier des joints individuels. Après vérification de la loi de réciprocité (noircissement proportionnel à l'exposition), pour les rayonnements utilisés, ils ont mesuré, à différentes températures et après différents temps de recuit, les profondeurs de pénétration en volume et aux joints de grains. Ils ont utilisé des dépôts assez épais (2 μ) pour pouvoir appliquer avec sécurité la formule (1.1.3) dans le cas de la diffusion massique. Comme $c = c_0 \operatorname{erf} c[y/2\sqrt{(D_v t)}]$, si l'on détermine la profondeur y_{lv} à laquelle la concentration a une valeur fixeé c_l, la quantité $y_{lv}/2\sqrt{(D_v t)}$ est invariante; il en résulte que $y_{lv}^2 = k_1 D_v t$. De même, dans le cas des joints de grains, si l'on peut mesurer la profondeur limite y_{lj} à laquelle la concentration a une valeur fixe, c_l, on a:

$$y_{lj}^2 = k_2 \frac{D_v^{1/2}}{D_j} \sqrt{t}$$

Il est donc possible de calculer D_v et D_j, à condition de connaître k_1 et k_2, c'est-à-dire la loi reliant le noircissement limite fixé arbitrairement à la concentration. On peut utiliser une méthode comparable en tirant profit de la sensibilité des méthodes de comptage.[29]

BORISOV *et al.*[26] ont repris récemment le problème de la diffusion intergranulaire en mettant au point une nouvelle méthode de calcul dans laquelle on ne suppose plus que la concentration à l'interface de départ reste constante. Les auteurs ont pu, de cette manière, suivre pour la première fois *d'une manière continue* la cinétique de la pénétration de radioélément dans le volume des cristaux et dans les joints de grains. La réalisation expérimentale est extrêmement délicate: l'échantillon est porté en quelques minutes à la température de recuit par l'intermédiaire d'une résistance de molybdène (intensité du courant: 500–1000 A). Le compteur de Geiger est placé à quelques mm de l'échantillon, ce qui pose d'importants problèmes de refroidissement. L'activité est mesurée toutes les 5 ou 10 min. La forme de la courbe donnant l'activité globale de l'échantillon en fonction du temps permet de calculer les coefficients de diffusion en volume et dans les joints de grains. La méthode, appliquée à l'alliage Fe–3% Si, semble très sensible et très rapide (environ 3 hr pour une étude complète), mais il est nécessaire d'attendre la publication complète du mémoire pour pouvoir étudier avec soin les principes du calcul.

4.4. L'autodiffusion superficielle

La diffusion doit être très rapide à la surface libre des métaux. Les études consacrées à ce phénomène sont encore peu nombreuses et ont surtout eu pour objectif de montrer, d'une manière semi-quantitative, l'influence de l'orientation des plans cristallographiques sur la diffusion. Il suffit pour réaliser de telles expériences de déposer un isotope radioactif à la surface d'un métal et d'étudier l'extension de la source après diffusion.

Mathématiquement, le problème est assez difficile à traiter, car il faut alors résoudre l'équation de Fick sous sa forme bidimensionnelle:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right)$$

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Il est plus simple de passer en coordonnées polaires; on obtient ainsi:

$$\frac{\partial c}{\partial t} = \frac{1}{r}\left[\frac{\partial}{\partial r}\left(rD\ \frac{\partial c}{\partial r}\right) + \frac{\delta}{\partial \theta}\left(\frac{D}{r}\ \frac{\partial c}{\partial \theta}\right)\right]$$

ou, si la diffusion est isotrope:

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\ \frac{\partial c}{\partial r}\right),$$

équation qui n'a pas de solution simple. WINEGARD et CHALMERS[27] ont effectué quelques mesures sur l'autodiffusion de l'argent par la méthode autoradiographique. Une photométrie précise leur a permis d'atteindre l'ordre de grandeur du coefficient de diffusion en surface comparable au coefficient d'autodiffusion intergranulaire. HACKERMAN et SIMPSON[28] ont tenté d'atteindre une précision plus grande en mesurant la concentration en radioélément en fonction de la variable r. Les deux groupes d'auteurs semblent avoir mis en évidence une anisotropie marquée de la diffusion superficielle, suivant la nature des plans cristallographiques étudiés. Cette anisotropie doit grandement contribuer à compliquer la résolution de l'équation de Fick qui doit alors faire intervenir la variable polaire θ.

5. CONCLUSION. CHOIX DES MÉTHODES

Nous avons présenté dans cette mise au point l'état actuel des techniques d'étude de l'autodiffusion à l'aide des isotopes radioactifs. Le nombre même de ces méthodes montre qu'il n'en existe pas d'universelle et que chaque métal étudié pose un problème nouveau. Nous tenterons cependant de classer les différentes méthodes proposées surtout dans le cas de l'autodiffusion en volume, puisque l'autodiffusion intergranulaire et surtout l'autodiffusion superficielle ont jusqu'à présent donné lieu à un nombre assez restreint de méthodes d'étude.

(1) Si l'on veut mesurer des coefficients de diffusion supérieurs à 10^{-11}, la méthode la plus recommandable est la méthode de sectionnement (3.1).

(2) Pour des coefficients plus faibles, il faut faire appel aux techniques d'absorption.

(3) Si le radioélément utilisé émet des rayonnements *fortement absorbés*, on peut utiliser sans inconvénient la méthode simple de STEIGMAN *et al.* (3.2.1), ou, au besoin, la méthode de BUFFINGTON *et al.* (3.2.1). La méthode de GRUZIN (3.2.2) peut également donner de bons résultats, bien qu'elle pose de sérieux problèmes expérimentaux et soit moins sensible que les méthodes de comptage.

(4) si le rayonnement émis est *très faiblement absorbé*, on peut utiliser:

(a) soit la méthode de GRUZIN (3.2.2) avec la difficulté qu'il faut déterminer avec précision la pente d'une courbe

(b) soit la méthode de KRYUKOV et ZHOUKHOVITZKY (3.2.4) qui nécessite la fabrication de minces plaquettes, mais est, dans son principe, très rigoureuse.

(5) si l'absorption du rayonnement est *moyenne, ou très complexe*, la méthode de KRYUKOV et ZHOUKHOVITZKY (3.2.4) est particulièrement recommandée. Dans le cas où la fabrication de minces plaquettes est impossible, on peut faire appel à la méthode de ZHOUKHOVITZKY et GEODAKYAN. Notons que, même dans ce cas, la méthode de GRUZIN (3.2.2) peut rendre des services en utilisant l'équation complète. Mais il faut alors pouvoir déterminer le coefficient d'absorption, ce qui n'est pas possible dans le cas où le rayonnement émis est trop complexe.

(6) Enfin la méthode récente de ZHOUKHOVITZKY et GEODAKYAN (3.4) peut permettre de mesurer de très faibles coefficients de diffusion, à condition de connaître pour chaque métal l'électrolyte convenable.

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Améliorations dans l'Utilisation des Radiotraceurs pour l'Étude de l'Usure des Segments de Piston Méthode IFP-RA3—Bilan d'Usure

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Un gain très important de sensibilité est obtenu en collectant l'huile descendant vers le carter dans une gouttière montée au bas de la chemise.

On enregistre en continu la différence entre l'activité de cette huile, et celle de l'huile du carter, par laquelle est alimentée la segmentation. La courbe obtenue traduit les variations du taux d'usure instantanée, et son intégration dans le système de coordonnées volumes d'huile-activité, fournit les valeurs de "l'usure apparente", contenue dans l'huile.

Le bilan complet de l'usure dans toutes les voies possibles, huile, segmentation, échappement, donne pour différents types d'huile, le coefficient dont il faut affecter l'usure apparente, pour obtenir "l'usure réelle", ou totale.

IMPROVEMENTS IN THE USE OF RADIOTRACERS FOR STUDYING WEAR IN PISTON SEGMENTS

By collecting the oil moving down to the sump in a gutter at the bottom of the liner, a great improvement in sensitivity is obtained.

The difference between the activity of this oil and that of the sump oil, by which the ring belt area is fed, is continuously registered. The curve obtained represents the variations of instantaneous wear-rate, and by integrating the graph of oil volume versus activity, we can obtain the "apparent wear", as carried in the oil.

A complete balance of wear in every possible direction (oil, rings, grooves and exhaust) gives for different types of oil the coefficient to be applied to "apparent wear" to obtain "real wear", or total wear.

УСОВЕРШЕНСТВОВАНИЕ ИЗОТОПНОГО МЕТОДА ИССЛЕДОВАНИЯ ИЗНОСА ПОРШНЯ

Достигнуто большое увеличение чувствительности метода путем отбора проб масла перед стеканием его в картер из специальных канавок в нижнем конце гильзы.

Разность между активностью этого масла и масла, находящегося в картере двигателя и питающего пояс колец непрерывно регистрируется. Полученная кривая соответствует изменениям мгновенной скорости износа. Интегрируя кривую зависимости между объемом масла и его активностью, можно получить величину "кажущегося износа" по содержанию продуктов износа в масле.

Сведением полного баланса, с учетом продуктов износа, как находящихся в масле, на кольцах и в кольцевых канавках, так и уносимых с выхлопными газами, можно получить коэффициент для подсчета реального или полного износа из величины "кажущегося износа" для различных типов масел.

VERBESSERUNGEN BEI DER VERWENDUNG VON RADIOISOTOPEN ZUR UNTERSUCHUNGSMETHODE IFP-RA3 FÜR ABRIEB VON KOLBENRINGEN UND BILANZ DER ABNÜTZUNG

Eine bedeutend höhere Empfindlichkeit kann erhalten werden, wenn das Öl mit Hilfe einer Rinne, die am Grund des Gehäuses montiert ist, gesammelt wird bevor es in den Carter zurückfliesst. Der Unterschied in der Aktivität dieses Öles verglichen mit der des Öles im Carter, durch welches die Kolbenschmierung gespeist wird, wird laufend registriert. Die erhaltene Kurve zeigt die Veränderung des Ausmasses des augenblicklichen Abriebs, ihre Integration im System der Volumskoordinaten der Ölaktivität ergibt die Werte des "augenscheinlichen Abriebs", welcher im Öl zurückgehalten wurde.

Eine vollständige Bilanz der Abnützung, die auf allen möglichen Wegen erfolgt, (im Öl, in den Kolben, durch Entwiechen) gaben für verschiedene Ölsorten jenen Koeffizienten, welcher auf die augenscheinliche Abnützung angewendet werden muss um die totale oder "reelle Abnützung" zu erhalten.

La méthode mesurant l'activité des parcelles métalliques libérées dans l'huile par l'usure d'un segment de piston radioactivé a remplacé, depuis plusieurs années déjà, les méthodes classiques, pesée, mensuration ou analyse chimique de l'huile, en raison de ses avantages importants: très grande sensibilité des appareils de mesure, permettant des essais brefs (quelques heures). Pas de nécessité de démontage entre essais successifs. Sélectivité parfaite: l'usure mesurée ne provient que de la pièce activée. Possibilité d'enregistrement en continu de l'activité, donc de l'usure, permettant l'investigation détaillée de phénomènes transitoires.

Dans l'application de cette méthode, il fût de pratique courante, jusqu'alors, de faire circuler l'huile, pompée puis recyclée au carter, devant un appareil de détection, sensible au rayonnement émis par l'élément actif dispersé dans l'huile (Fig. 1(a)).

Dans ces conditions, les usures s'additionnant dans l'huile, au cours de l'essai, pour un taux d'usure horaire constant, on obtient pour courbe d'enregistrement une droite dont la pente représente ce taux horaire.

La Fig. 1(b) donne l'allure classique de la courbe pratique d'un essai. On la traduit généralement en mg d'usure en comparant l'activité de l'huile à celle d'une solution étalon contenant une concentration connue de l'élément actif utilisé, à la même activité spécifique que dans le segment.

Il nous est apparu cependant que ce mode opératoire présente un défaut de sensibilité dans son principe, puisque l'on mesure l'activité des particules d'usure, en quantité toujours faible, après les avoir disséminées

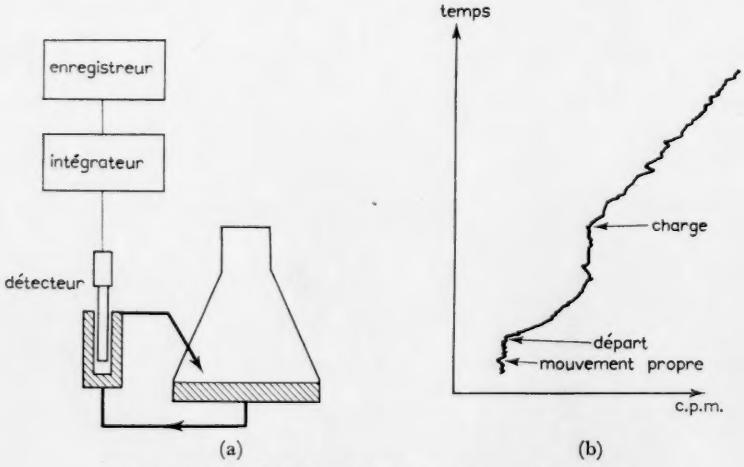

FIG. 1. Méthode classique (a) schema, (b) type de courbe.

dans la charge totale d'huile de l'installation, c'est-à-dire sur une suspension très diluée.

Pour remédier à ce vice de principe, nous avons élaboré une nouvelle méthode, dénommée Méthode IFP-RA3, que nous allons décrire ci-après.

1. METHODE IFP-RA3

A. Principe

Afin d'éviter la dilution de l'usure dans la charge totale d'huile, nous avons muni notre moteur d'essai d'un système de gouttières, à la base de la chemise (photo Fig. 3).

L'huile "descendante" sur la paroi du cylindre vient tomber dans ces gouttières, d'où elle est reprise par une pompe, et refoulée dans un serpentin disposé autour d'un cristal scintillateur, duquel elle s'écoule dans des éprouvettes graduées permettant de mesurer les volumes d'huile recueillis dans les divers laps de temps successifs d'un essai.

Pratiquement, nous n'avons pu mettre en place que deux demi-gouttières, séparées par un espace nécessaire au passage de la bielle dans son mouvement de balancier. Ceci entraîne qu'une fraction de l'huile descendante, de l'ordre de 40 pour cent, retourne au carter directement.

L'huile recueillie dans l'éprouvette graduée, à sa sortie du serpentin de comptage, ne peut être purement et simplement recyclée au carter. Dans ce cas, en effet, une fraction inconnue de l'usure, déjà comptée, repasserait dans la zone de la segmentation, et serait de nouveau comptée; l'interprétation de la courbe enregistrée serait impossible.

Or, l'importance des volumes recueillis, de l'ordre de 1000 ml/hr nécessite l'apport au carter, pour y maintenir le niveau, soit d'une quantité équivalente d'huile neuve, soit de l'huile recueillie elle-même, débarassée de son activité, ou directement, moyennant certain dispositif.

L'apport d'huile neuve présente l'inconvénient de régénérer pratiquement l'huile tout au long de l'essai et ne permet pas l'étude de l'évolution des qualités anti-usure d'un lubrifiant.

L'élimination des parcelles actives dispersées dans l'huile est difficile, en raison de leur extrême finesse et de la viscosité du milieu. Elle nécessite (après abaissement de la viscosité par dilution dans un solvant) la mise en oeuvre successive de filtres magnétiques, et de filtration sous pression sur lits de poudre de verre ultra-fine, puis la distillation du solvant, opérations longues, permettant difficilement de traiter 1000 ml/hr.

On fut donc amenés à recycler l'huile active elle-même; la difficulté mentionnée ci-dessus fut écartée, en exécutant un deuxième comptage d'activité, en continu sur l'huile du carter, c'est-à-dire sur l'huile qui alimente le film sur la chemise.

On opére donc en fait deux comptages simultanés, l'un sur l'huile "montante", l'autre sur l'huile "descendante" et l'on retranche en continu la première activité de la deuxième. La difference représente à tout instant l'activité gagnée par l'huile lors de son transit dans la zone de segmentation, et elle est donc proportionelle à l'usure instantanée du segment qui s'est manifestée quelques instants auparavant.

Pratiquement, les impulsions délivrées par les deux détecteurs sont transmises à deux intégrateurs identiques, dont la différence des tensions de sortie alimente un potentiomètre enregistreur (Fig. 2(a)). Le temps de réponse de l'installation, de l'ordre de 3 min est le temps nécessaire pour véhiculer l'huile de la segmentation et du carter, jusqu'aux détecteurs.

La situation des appareils de comptage par rapport au segment actif, et les volumes des deux serpentins les entourant, sont tels que, vides de toute huile, ou pleins d'une même huile active, les mouvements propres et les taux de comptage respectivement sont égaux. Les différences correspondantes sont donc nulles.

B. Type de courbe obtenue

La différence d'activité entre huile descendante et huile montante étant proportionelle à l'usure instantanée du segment, pour un

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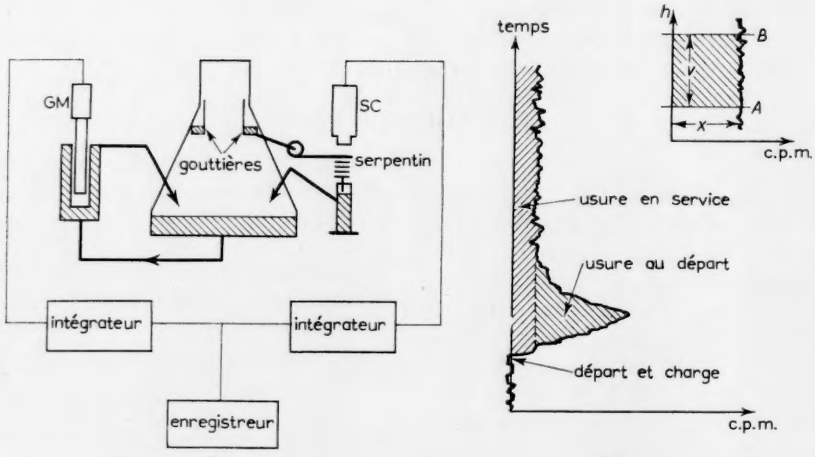

(a) (b)

FIG. 2 . Méthode IFP-RA3 (a) schema, (b) type de courbe.

taux d'usure constant, la courbe d'enregistrement est une verticale (Fig. 2(b)). Avant démarrage, on laisse inscrire pour contrôle la verticale de mouvement propre, dont l'abcisse moyenne doit être nulle. Environ 3 min après lancement et mise en charge du moteur, on note une brutale augmentation d'activité différentielle, due à l'arrivée dans le serpentin de gouttière du tampon d'huile chargé de l'usure au départ. A mesure que ce tampon s'élimine, l'activité redescend, suivant le taux d'usure, et se stabilise suivant une verticale.

C. Interprétation de la courbe

Considérons un tronçon de courbe AB vertical, correspondant à un temps de fonctionnement t_{AB}, et à un volume d'huile V recueilli à l'éprouvette (Fig. 2(b)).

A chaque instant, l'abscisse x cpm de la courbe représente l'activité de y mg de parcelles d'usure libérées dans l'huile à la segmentation, en sus de celles déjà présentes dans l'huile montante, et réparties dans le volume v (47 ml) du serpentin de gouttières.

La valeur Y mg de l'usure libérée dans l'huile à la segmentation pendant le temps t'_{AB}, égal à t_{AB} mais décalé en avance de 3 min, sera $Y = y \cdot \dfrac{V}{v}$.

En passant, après essai, une solution étalon dans le serpentin de gouttière, on détermine l'abscisse X de l'activité due à la présence dans ce serpentin de la masse Z connue de fer de segment actif, contenue dans v ml de solution étalon.

On peut donc déterminer $y = Z \cdot \dfrac{x}{X}$ d'où Y.

En pratique, on détermine chaque jour, grâce à la solution étalon, le poids p mg de fer de segment, nécessaire dans le serpentin de gouttières pour obtenir 100 cpm à l'enregistrement.

Puis on "intègre" l'activité totale A gagnée par l'huile à la segmentation pendant le temps t'_{AB}, et enregistrée le long de AB:

$A = x \cdot \dfrac{V}{v}$ et l'on obtient alors $Y = \dfrac{A}{100} \cdot p$.

Les courbes d'enregistrement présentent en réalité de nombreuses fluctuations autour de verticales moyennes: certaines de faible amplitude (10 cpm) sont dues à l'aspect statistique du rayonnement. D'autre, plus importantes sont liées aux variations d'usure causées par les rencontres de pics des états de surface du segment et de la chemise, qui rompent localement le film d'huile amenant des grippages partiels ("Scuffing"). Ces derniers s'amoindrissent à mesure que le segment et la chemise sont mieux rodés.

Pour interpréter, comme nous venons de le voir, cette courbe fluctuante, on "moyenne"

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FIG. 3. Photographie des gouttières.

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chaque tronçon correspondant à un volume d'huile recueilli connu, et particulièrement le "pic" d'usure au départ.

La masse totale d'usure gagnée par l'huile durant tout l'essai, ainsi déterminée, est inférieure à la masse présente dans la charge totale d'huile en fin d'essai calculée à partir de l'activité d'un prélèvement fait au carter à l'issue de l'essai. La différence représente la fraction déjà signalée (40 pour cent) retombée directement au carter, et sa connaissance permet de déterminer un coefficient de correction C_1 dont il faut affecter les usures déterminées sur la courbe, pour obtenir les usures véritables correspondantes, libérées dans l'huile.

*D. Avantages de la méthode IFP RA*3:

Cette méthode, présente à notre sens, les avantages suivants, par rapport à la méthode classique:

(1) A activité spécifique du segment égale, le facteur de gain de sensibilité est de l'ordre de 20 à 30.

(2) Du fait de la plus forte concentration du fer dans l'huile "descendante", les variations de taux d'usure sont mieux marquées. De plus, des variations d'abscisse sont plus aisément et rapidement lisibles que des variations de pente. L'étude de phases transitoires et particulièrement de "l'usure au départ", s'en trouve facilitée.

(3) En supposant enfin, que la concentration en fer de l'huile descendante est homogène, de la fraction d'usure retombée au carter, on peut déduire le volume d'huile qui l'a véhiculée. En l'ajoutant au volume pompé aux gouttières, on obtient le volume total ayant "transité" dans le film au cours de l'essai, qui peut aider à l'interprétation de certains phénomènes.

2. BILAN DE L'USURE

Nous nous sommes posés la question de savoir si l'usure vehiculée par l'huile et mesurée jusqu'alors représentait la totalité de l'usure réelle, ou seulement une fraction, "usure apparente".

Dans cette hypothèse il fallait connaître quelles seraient la valeur de cette fraction, et, les voies d'évacuation possible de l'usure, en dehors de l'huile, et savoir si leur capacité d'absorption serait la même selon les natures d'huile, et particulièrement selon leur détergence.

Ce problème se posait comme préalable à l'expérimentateur désireux de comparer valablement entre elles des huiles de natures détergentes différentes. Les "coefficients d'usure apparente" pouvaient en effet différer d'une huile à une autre, entrainant des classements basés sur ces usures apparentes non conformes à la réalité.

Une première série d'essais, sur une même huile, avec détermination par pesée de la perte pondérale, nous a montré que la perte déterminée par comptage représentait toujours une fraction de l'ordre de 70 pour cent de la perte déterminée par pesée.

Une autre série d'essais, sur des huiles différentes, nous ayant montré que la valeur de cette fraction variait effectivement d'une huile à une autre, nous avons mis au point un mode opératoire et des agencements spéciaux permettant de déterminer le montant de l'usure dans toutes les directions possibles:

(1) Huile pompée aux gouttières	Fer dans l'huile (usure apparente)
(2) Retombées directes au carter	
(3) Usure retenue sur les segments	Fer hors de l'huile
(4) Usure retenue sur le piston	
(5) Usure entraînée à l'échappement	

leur total, constituant l'usure réelle.

Ces bilans ont été réalisés pour 3 huiles de degré de détergence différents. Les résultats d'essais sont groupés dans le tableau 1, où l'on trouve en valeurs absolues, et en pour cent les usures totales et par voies,

déterminées par comptage, comparées aux usures totales déterminées par pesée.

On retrouve toujours, par comptage, à quelques pour cent près par défaut, les usures pondérales, ce qui prouve que les dispositifs utilisés pour récupérer le fer entraîné à l'échappement laissent encore la place à quelques pertes. L'écart maximum est de 5,2 pour cent et l'écart quadratique moyen de 7,8, ce qui est une précision assez remarquable si l'on tient compte du fait que les manipulations intéressaient des masses de métal de l'ordre de la fraction de mg, disséminées dans le complexe de pièces mécaniques et de cambouis d'un moteur Diesel.

Il ressort que les usures apparentes mesurées par comptage sur l'ensemble gouttières–carter, représentent des fractions de l'usure réelle, de l'ordre de 82 pour cent pour une huile non dopée, et de 74 pour cent pour une huile détergente.

Encore que cette différence soit faible, elle méritait d'être connue, et d'autre part, elle paraît étonnante au prime abord. On pensait en effet qu'une huile détergente, maintenant le moteur plus propre, devait véhiculer vers les gouttières et le carter une fraction plus importante de l'usure, donnant un coefficient d'usure apparente plus élevé que pour une huile minérale pure.

La réalité se trouve être inversée et s'explique ainsi:

Les additifs détergents manifestent toujours, plus ou moins, des qualités antiusure, et les huiles les renfermant, donnent,

TABLEAU 1

Type d'huile	Non détergente			Détergente			Détergente–Multigrade		
Gouttières	12,3	12,9	8,1	3,2	3,9	1,8	1,64	2,14	1,01
Carter	3,9	3,4	3,6	1,8	1,3	0,8	0 3	0,78	0,45
Total (mg)	16,2	16,3	11,7	5	5,2	2,6	1,94	2,92	1,46
Segments	0,89	0,73	0,52	0,47	0,49	0,13	0,16	0,55	0,08
Piston	0,68	0,76	0,62	0,14	0,10	0,10	0,08	0,12	0,02
Echappement	1,03	0,94	1,18	0,85	0,52	0,59	0,43	0,32	0,15
Total (mg)	18,80	18,73	14,02	6,46	6,31	3,42	2,31	3,91	1,71
Pesée (mg)	19,2	20,0	14,4	6,9	6,9	3,5	2,7	4,2	1,9
Durée (hr)	8,50	8,50	5	8,50	7,75	5	7,50	7,50	5
Gouttières	64	65	56	47	57	52	61	51	53
Garter	20	17	25	27	19	22	11	19	23,6
Total (%)	84	82	81	74	76	74	72	70	76,6
Moyenne	82,5			75			73		
Segments	4,6	3,6	3,6	6,8	7,1	3,7	6,1	13	4,3
Piston	3,6	3,8	3,8	2	1,6	2,8	3,1	2,9	1,2
Echappement	5,4	4,7	4,7	12,4	7,6	17	16	7,6	7,6
Total (%)	13,6	12,1	16,1	21,2	16,3	23,5	25,2	23,5	13,1
Moyenne (%)	13,9			20,2			20,6		
Total (%)	97,6	94,1	97,1	95,2	92,3	97,5	97,2	93,5	89,7

Pour l'avant dernière colonne, l'essai a été mené sur un nouveau segment, non rodé: il en résulte un taux d'usure plus élevé.

à durée d'essai égales, des pertes beaucoup moins fortes que les huiles non dopées. Il semble, par ailleurs, que la segmentation, et plus particulièrement encore l'échappement, présentent une certaine capacité de rétention ou d'absorption des parcelles d'usure; cette capacité se trouve bien diminuée par la détergence de l'huile, mais dans une proportion moindre que se trouvent renforcées les qualités anti-usure. Il en résulte que, pour les huiles détergentes, la fraction d'usure "hors huile" (segments + piston + échappement) est de l'ordre de 20 pour cent, contre 13 pour cent pour les non détergentes. Corrélativement, ceci entraîne que la fraction d'usure apparente "dans l'huile" est plus importante pour l'huile non détergente contrairement aux prévisions.

CONCLUSION

Nous avons le sentiment d'avoir largement prouvé, dans ce travail, la validité et les possibilités de cette nouvelle méthode.

Les essais menés sur une huile se traduisent maintenant par une valeur d'usure au départ et une valeur de taux horaire d'usure en régime stabilisé, déduites de la courbe d'enregistrement. Ces valeurs, affectées d'un coefficient C_1 déterminé en fin d'essai, donnent "l'usure apparente". Un deuxième coefficient C_2, pris égal à 0,82 pour une huile minérale pure, et égal à 0,75 pour une huile détergente, ou, pour plus de précision, déterminé par un bilan, permet de passer de l'usure apparente à "l'usure réelle" qui tient compte de toutes les voies de répartition possible de l'usure.

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Tracing of Water Flow by means of Radioactive Isotopes and Scintillation Counters*

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Radioactive isotopes have been employed for determinations of residence times in sewage purification plants and also for investigations on flow patterns and dilutions in large natural waters such as lakes and river mouths because of the ever increasing use of such systems for the discharge of waste water.

In the latter investigations, emphasis was laid on the use of γ-emitting short-lived tracers such as Na^{24} and Br^{82} in combination with submerged scintillation counters. This combination gives such a high sensitivity that the direct assay of concentrations of only 10^{-7} c/m^3 could be easily performed. The high sensitivity of the method is due to the large volume contributing to the signal, the high radiation absorption probability in the detector and the reduction of the background counting rate. The measurements have been carried out from small boats equipped with two-way radios, position determining instruments and battery-operated scintillation counters. Flow patterns in receivers of more than 10^8 m^3 volume have been obtained within 10–20 hr with about 1 c of tracer. The use of short-lived tracers and the rapid dilution produced during the experiment eliminated all health hazards due to radiation except for the easily controllable external exposure occurring during the handling of the radioactive material.

L'OBSERVATION DE L'ÉCOULEMENT DE L'EAU AU MOYEN DES ISOTOPES RADIOACTIFS ET DES COMPTEURS À SCINTILLATION

Les isotopes radioactifs ont servi aux mesures des périodes de demeure dans les installations à purification des eaux d'égout, ainsi que dans les recherches sur les modèles d'écoulement et sur les dilutions dans les grandes étendues d'eau naturelles telles que les lacs et les embouchures de fleuves, vu l'emploi toujours croissant de tels systèmes pour décharger les eaux de rebut.

Dans ces dernières recherches, l'insistance fut mise sur l'emploi des indicateurs émetteurs de γ de courte vie, tels que la Na^{24} et le Br^{82}, combiné à celui des compteurs à scintillation submergés. Cette combinaison donne une sensibilité si élevée que le dosage direct de concentrations de seulement 10^{-7} c/m^3 a pu facilement s'achever. La sensibilité élevée de la méthode suit de la grandeur du volume contribuant au signal, de la forte probabilité d'absorption de radiation dans le détecteur et dans la diminution du taux du compte de base. Les mesures se sont faites en employant de petits bateaux portant radiotéléphone, indicateurs de position et

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compteurs à scintillation fonctionnant à piles. On a achevé des modèles d'écoulement dans des récipients de plus de 10^8 m^3 de capacité dans 10–20 hr avec environ 1 c d'indicateur. L'emploi des indicateurs de courte vie et la dilution rapide qui se produisait durant l'expérience élimina tout danger à la santé venant de la radiation sauf l'exposition extérieure, facile à contrôler, qui a lieu lors de la manipulation du matériel radioactif.

ИЗУЧЕНИЕ ВОДНЫХ ПОТОКОВ ПРИ ПОМОЩИ РАДИОАКТИВНЫХ ИЗОТОПОВ И СЦИНТИЛЛЯЦИОННЫХ СЧЕТЧИКОВ

Радиоактивные изотопы применялись в установках по очистке сточных вод для определения времени нахождения загрязнений в воде, а также для исследования распределения и перемешивания потоков в больших природных бассейнах, например, в озерах или в устьях рек, которые все чаще используются для спуска сточных вод.

В последнем случае применялись в основном короткоживущие изотопы с гамма-излучением, как например Na^{24} и Br^{82}, с одновременным использованием погруженных в воду сцинтилляционных счетчиков. Такая комбинация обеспечивает высокую чувствительность, позволяющую легко определять столь малые концентрации как 10^{-7} кюри/м^3 и обуславливаемую большим объемом среды, из которой поступают импульсы, большой вероятностью поглощения излучения детектором и уменьшением фона. Измерения производились с маленьких лодок, снабженных двухсторонними радиопередатчиками, приборами для определения положения и сцинтилляционными счетчиками с питанием от батарей. Передатчики давали полную картину распределения потоков в 10^8 м^3 в течение 10–20 часов, при I кюри изотопа. Применение короткоживующих изотопов и быстрое их разбавление во время опыта исключали всякую опасность от излучения, если не считать опасности от непосредственных манипуляций с радиоактивным материалом, против которой легко принять соответствующие меры.

UNTERSUCHUNG VON WASSERSTRÖMUNGEN MIT HILFE VON RADIO-ISOTOPEN UND SZINTILLATIONSZÄHLERN

Radio-Isotopen wurden sowohl zur Untersuchung der Verweilzeit won Wässern in Kläranlagen, wie auch zur Feststellung des strömungsweges und der Verdünnung in grossen natürlichen Gewässern, wie z.B. Seen und Flussmündungen, verwendet, da solche Systeme in steigendem Masse zur Beseitigung von Abwässern herangezogen werden. Bei diesen Untersuchungen wurden vor allem kurzlebige γ-Strahler, wie z.B. Na^{24} und B^{82} zur Markierung und tauchbare Szintillationszähler verwendet. Diese Kombination ergibt eine hohe Empfindlichkeit, so dass Direktmessungen von Konzentrationen von nur 10^{-7} c/m^3 leicht durchgeführt werden konnten. Die hohe Empfindlichkeit der Methode beruht auf dem grossen Volumen, das für die Messung wirksam wird, auf der hohen Absorptionswahrscheinlichkeit des Detektors für die Strahlung und auf der Herabsetzung der Hintergrundstrahlung. Die Messungen wurden von kleinen Booten aus durchgeführt, welche mit Gegensprechanlage, Positionsbestimmungsinstrumenten und batteriebetriebenen Szintillationszählern ausgerüstet waren.

Stromungswege in Gewässern von mehr als 10^8 m^3 Volumen wurden innerhalb von 10–20 Stunden mit Hilfe von etwa 1 c erhalten. Die Verwendung von kurzlebigen Strahlern und die rasche Verdünnung des Tracers während des Experimentes verhindern jede Strahlungsgefährdung, abgesehen von der leicht kontrollierbaren äusserlichen Bestrahlung beim Hantieren mit dem radioaktiven Material.

INTRODUCTION

RADIOACTIVE isotopes have been used for the tracing of water flow in a series of investigations carried out during the last few years in Sweden.

Important contributions in this field have earlier been given by ARCHIBALD,[1,2] THOMAS,[2] ELY[3] and GOODMAN[4] in U.S.A., by MONTENS,[5] SAUERWEIN[6] and SONS[7] in Germany and by TRUESDALE[8] and PUTMAN *et al.*[9] in England.

In the investigations reported here, the residence times in sewage treatment plants of different constructions as well as the flow patterns in natural waters such as rivers, lakes and river mouths have been studied.

SEWAGE SETTLING TANKS (1 m³–100 m³)

Stocksund (1–2 m³)

In 1953, radioisotopes were used in Sweden for the first time to study the flow characteristics and mean retention times in sewage settling tanks.[10] The effluent from about 300 houses in Stocksund near Stockholm is purified in an experimental plant consisting of about 20 different tanks. These tanks are of the "chamber" and "emscher" types. $Rb^{86}Cl$ (19 days half-life) was chosen as tracer and the tracer solution was added all at once to the inlet. The Rb^{86}-concentration of samples taken in the outlet was measured with a jacketed Geiger-Müller tube and a scaler.

Fig. 1 shows some results. The sewage water passed more rapidly through the emscher tanks than through the chamber tanks. A purification tank should possess a long residence time in order to have a good purification capacity. The results obtained here were therefore of great value for the comparison of different tank constructions.

Hällberga, Tystberga, Jönåker (100 m³)

Three large settling tanks for the purification of effluent from larger communities were investigated in 1954.[11] The tank volumes were about 100 m³. In these investigations, scintillation counters were used together with Geiger-Müller tubes. The scintillation counter was equipped with a water-tight probe.[12] Fig. 2 shows some results from activity measurements on the outlet from a cylindrical well tank. It is seen that, in this case, part of the labelled water passed through the tank in a very short time. The theoretical retention period is about 10 hr but, after only 2 hr, it was found that 70 per cent of the rubidium had flowed through. This indicates a poor purification efficiency.

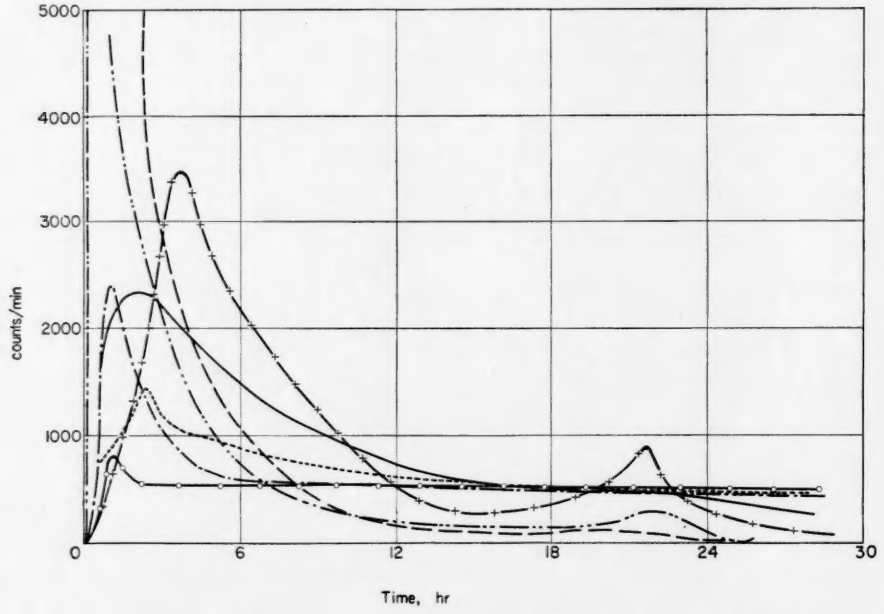

FIG. 1. Activity in the outlets of seven tanks at different times after the addition of Rb^{86} Cl to the inlets.

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LARGE NATURAL RECEIVERS

A series of investigations on the outlets of rivers into large receivers has been performed during the last two years, all of which have used scintillation counters for activity determinations *in situ*.

The investigations have many features in common and the technical details will therefore not be repeated in all cases.

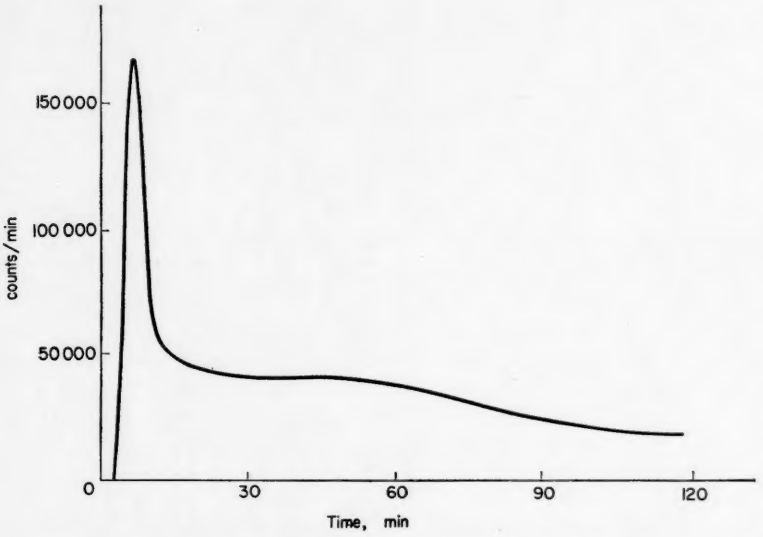

FIG. 2. Concentration of radioactive $Rb^{86}Cl$ in the outlet of a sewage settling tank shaped like a cylindrical well. The theoretical residence time was about 10 hr but it is seen that, after only 2 hr, about 70 per cent of the rubidium had already passed.

Svartvik

The first large-scale investigation was made in the Svartvik fjord at the outlet of the Ljungan river in the Gulf of Bothnia. A pulp mill situated at the fjord uses the Ljungan water flow, 70–100 m^3/sec, for the dilution and discharge of waste water. It was considered likely that a discharge of effluent at a depth of 20 m close to the outlet would ensure a considerable and rapid dilution and a rapid transport towards the sea.

The radioactive substance, which in this case consisted of 100 mc irradiated sodium bicarbonate (Na^{24}; half-life 15 hr), was dissolved in 5 m^3 waste water in a tank. The contents of the tank were then pumped out at a depth of 20 m over a period of 6 min.

During the next few hours, measurements of the activity distribution in the water mass of the fjord were made from two small tugboats by means of scintillation counters. Fig. 3 shows the activity distribution in a vertical plane along the direction of flow about 1 hr after the injection. No measurements were made at the same time in the vicinity of the injection point but measurements at later stages showed that a certain amount of activity still remained here.

The measurements showed that, if all the effluent from the mill were continuously discharged at the point chosen, the rate at which effluent were to be pumped out would be greater than the dilution rate. An accumulation would thus result making the intended outlet at this point unsuitable.

Emån

In the planning of a sulphate factory near the mouth of the Emån river on the Baltic, information was wanted on how a reduction of the fresh-water flow caused by the water

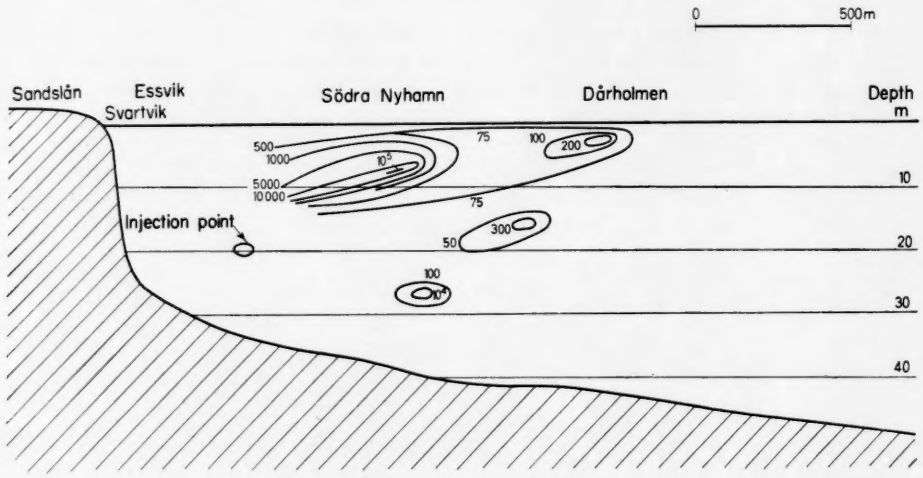

FIG. 3. Activity distribution in a vertical plane along the flow direction in the Ljungan river about 1 hr after the addition of radioactive tracer. Iso-count curves have been drawn using counts/min.

consumption of the mill would affect the mixing of the fresh water and salt water close to the river outlet because of its effect upon fish migration.

The investigation was made using 100 mc NH_4Br^{82} as tracer in each experiment. The salt solution was kept in a glass carboy which was shattered at the most suitable point in the river mouth. This point was established in a preliminary experiment using sodium fluorescein. The measurements were made from boats equipped with scintillation counters. When evenly distributed in 10^6 m^3, the 100 mc of Br^{82} gave a net count rate of about 50 counts/min which is approximately equal to the background count rate with the scintillation probe at a 1 m depth. As a result of the experiments, it was found that the wind had a much stronger influence on the mixing pattern than a variation in the water flow.

Mariestad

The water flow patterns in two bays in the Lake Vänern, the largest lake in Sweden, have been studied. In the first investigation, the purpose was to determine the flow path and the spread into the lake water of the water from the Tidan river.

This river which flows out into the Mariestad fjord carries the waste water from factories situated along the river.

The volume of the fjord was estimated to be $0{\cdot}8 \times 10^8$ m^3. Because of this large volume, an amount of 0·6 c of Br^{82} as NH_4Br was used as tracer.

The injection method was the same as that mentioned above and the measurements were carried out from three small boats equipped with scintillation counters. The radioactivity distribution was mapped over an area of 10 km^2 both in this and the following investigation and this necessitated the determination of the position of the measuring points. For this purpose, angle readings to fixed points on land were taken. The boats were also equipped with walkie-talkies for internal communication, which made it possible to follow the tracer over this large area with only three boats, without any risk that essential parts of the process were lost.

The result of the investigation in the Mariestad fjord is partly shown in Fig. 4. By means of iso-count curves drawn for suitable periods of time, usually 1 hr, the spreading and dilution can be demonstrated. To start with, the tracer moved slowly to the

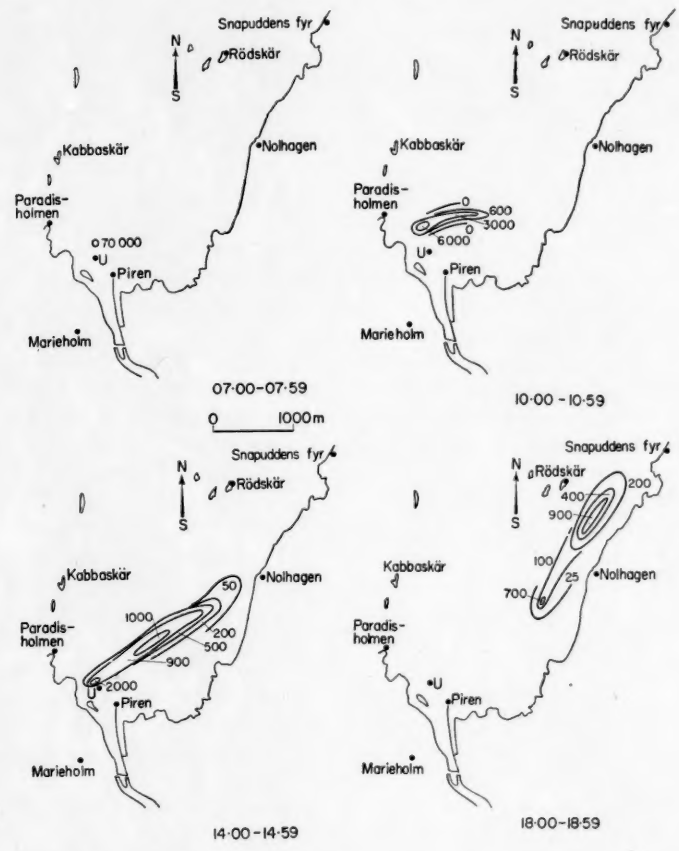

FIG. 4. Flow path and spreading of radioactive salt (NH_4Br^{82}) in the Mariestad fjord. The force of the wind was 3–4° Beaufort from S.W. The injection was made at 07·00 hr at the point marked U. The activity was measured in counts/min.

north under the influence of the river water, the volume flow of which was 38 m^3/sec on the day of the experiment. Thereafter the path was mainly determined by the wind and the topography of the bottom of the fjord.

The second investigation was similar to the first one. In this case 1 c of Br^{82} was used in a water volume of $2{\cdot}5 \times 10^8$ m^3.

DISCUSSION

Choice of tracer

The choice of tracer depends on many factors. In the applications described above, the health hazards are the prime consideration. Therefore, one works with as short-lived isotopes as possible of elements with low toxicity. In most investigations, Na^{24} and Br^{82} with 15 and 36 hr half-life respectively have been used since it has been found sufficient to follow the active water mass for one or two days only. These nuclides emit γ-radiations with 2 and about 3 γ-photons per disintegration, respectively, and are very suitable for scintillation counter detection.

If a longer half-life is needed, Rb^{86} with 19 days half-life offers greater possibilities. Rubidium-86 emits hard β- and γ-radiation. The γ-radiation corresponds, however, to only about 10 per cent of the disintegrations and therefore this isotope is less suitable for γ-counting but it is still very useful for the determination of residence times in tanks, and other vessels of not too large volume, especially when β-counting of the samples is used.

The chemical properties of the tracer must also be taken into consideration. It is impotrant to choose a tracer which is not lost by adsorption on various surfaces. Alkali metal ions and monovalent anions in low specific activities are therefore preferred. In the investigations reported above on settling tanks, the recovery of rubidium was investigated and was found to be more than 90 per cent, proving that no substantial sorption of rubidium took place.

Other investigations on large receivers have been made with other nuclides. Scandium-46 was used in U.S.A. to study the dilution of waste water in the Santa Monica Bay outside Los Angeles with a continuous tracer admixture to the waste water for about 1 hr.[3,4]

Tritium-labelled water as a tracer would completely eliminate all risks for losses due to adsorption but the cost of the tritium tracer and measuring instrument would be much higher. Furthermore, the great advantage of obtaining immediate results, which greatly reduces the work involved, would be lost. Bacterial tracers have also been used by other experimenters.[9]

Calculation of the necessary amount of tracer

In investigations of this kind, it is necessary to decide how long, i.e. to what dilution, one wishes to follow the tracer. Then experience or theoretical considerations will give the approximate amount of tracer required. The count rate from a uniformly radioactive solution can be conveniently calculated from a formula given by Anianssson and Erwall.[13]

If a radioactive substance is uniformly distributed in a very large volume at a concentration of n disintegrations per min and cm^3, $N = nA/4\ \mu$ particles or photons per min will cross an area of A cm^2 where μ is the linear absorption coefficient in water expressed in cm^{-1}. The quantity registered, however, is $N' = \eta N$ where η is the absorption probability in the detector volume. For β-radiations, η is close to 100 per cent while, for γ-radiations, η varies within wide limits. For a sodium iodide crystal, 1 in. diameter $\times$ 1 in. thick ($A = 25$ cm^2), η is about 40 per cent for a 1 MeV γ-radiation and $\mu = 0{\cdot}07$ cm^{-1}. Thus one obtains $N' \approx 80$ counts/min for a concentration of 1 c of this tracer in 10^6 m^3 (2·2 dpm/cm^3). In practice, this value is approximately doubled due to the build-up which has not been taken into account in the formula.

The detectors

The investigations reported above have shown the importance of continuously registering the activity with counting rate meters since the process studied can be immediately monitored and unnecessary measurements eliminated. The formula quoted above for counting rate calculations shows that, for high sensitivity, γ-radiating tracers should be used in order to keep the value of the absorption coefficient small. The choice of a scintillation detector is then natural. The use of large Geiger-Müller tubes would also be possible since the increase in area (A) would compensate for the smaller absorption efficiency (η) but the handling of such large tubes would be less convenient in practical work, especially when measurements are to be carried out at large depths. The scintillation detector also accepts, without loss of counts, the high counting rates occurring in the first phase of the experiments.

In our experiments, two types of scintillation counters have been used, viz. the Model 389 H Super Scintillac Counter of the Victoreen Instrument Co. (battery operated) and the above-mentioned detector probe together with a Model 410 Count Rate Meter of the Atomic Instrument Co. (mains operated, requires generator). The sodium iodide crystals in the two detectors are 1·5 in. diameter $\times$ 1·25 in. thick and 1 in.

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diameter × 1 in. thick respectively. The probes are water- and pressure-tight. The probe of the Victoreen instrument can be connected to the rate meter through any length of cable, thus making possible activity measurements at very large depths.

The background

The sensitivity of the method is determined by the background counting rate of the instrument. This originates from cosmic and terrestrial radiation. Usually, the background counting rate of a scintillation detector is considerably higher than that of a Geiger-Müller detector, which is a disadvantage of the former detector. However, when measurements are made with the detector submerged in water, the background is reduced by the screening effect of the water. This is illustrated in Fig. 5 where the background counting rate is given for a scintillation counter with an energy discrimination at about 100 keV. The counting rate is nearly constant from 1 m under the surface down to 1 m from the bottom. The value is 40 counts/min which indicates a drastic reduction compared with the value 1500 counts/min measured on land. The curve also shows that the terrestrial γ-radiation constitutes a larger part of the background than the cosmic radiation. This curve has been found to be valid in all measurements in lake water. It appears as if the lowest attainable count rate in salt water is somewhat higher, probably due to the presence of radioactive salts. Further investigations of this phenomenon and of the spectral distribution of the background radiation as well as of the possible presence of free neutrons would be of great interest.

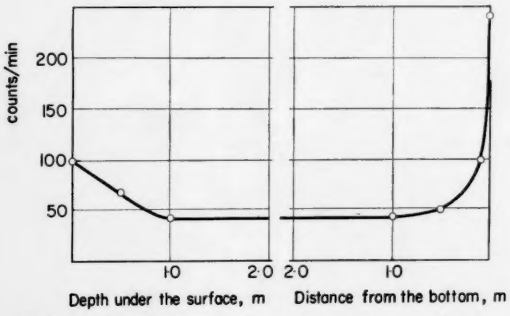

FIG. 5. The background counting rate of a scintillation detector in a lake. The background reading on land is about 1500 counts/min. The discriminator level was 100 keV.

The results also indicate that water in thicknesses of 1 m or more is a very efficient radiation shielding material. This might be of importance in the planning of low activity measuring facilities in nucleonic laboratories as well as for industrial tracer work.

Accuracy of the results

The activity measurements in flow pattern investigations are most conveniently collected together in iso-count maps with time periods of a duration equal to the time taken to scan the whole active area. This scanning may take a considerable time, when large areas are involved, with the limited number of measuring boats usually available and therefore it is evident that a distortion of the curve pattern will result from the continuous spreading of the tracer during the measuring period. Thus, the plotted iso-count contours cannot be regarded with the same confidence as the single activity and position determinations but do serve as a means for describing the tracer transport and dilution.

The object of the investigations reported here was to obtain a clear picture of the flow path in the receiver rather than precise data on the dispersion of the tracer. The measurements were planned with prime importance being attached to the determination of the boundaries of the active volume and with special consideration towards any possible branching of the flow and any local accumulation of activity. The areas scanned by the boats overlapped, to some extent, as a precaution against erroneous results and the missing of active volumes.

Future developments

As has been pointed out, a concentration of 1 c/10^6 m^3 of a 1 MeV γ-emitter gives a net count rate, when build-up is taken into account, of about 150 counts/min in a typical scintillation counter submerged to a depth of more than 1 m. This is still easily measurable on the rate meter since the

background level is about 50 counts/min.

The background counting rate might possibly be reduced somewhat but hardly enough to produce a significant increase in the sensitivity of the method. The result is that 1 (MeV) c can be detected in 5×10^6 m^3 *in situ*.

The amount of activity added can of course be increased. This is possible without producing prohibitive health hazards. Activities of up to 5 c of γ-emitters can be handled with simple equipment and transported in not too heavy containers. With special equipment it is possible to handle much more, which, for example, is shown in the Santa Monica investigation where 20 c of Sc^{46} were used.[4] With 20 c of Br^{82}, one should be capable of tracing a dilution to 3×10^8 m^3, which corresponds to the linear measures 10 m $\times$ 1000 m $\times$ 30,000 m.

A special technique, which has been used but not systematically tested, utilizes the "step-wise" addition of tracer. Here the flow is followed to a point where the dilution nearly reaches the detection limit and then a new addition of tracer is made.

When the sensitivity of the method presented here is not satisfactory, the possibility of using methods for concentrating the activity in the samples remains.

The use of continuous outlet of activity for a period of time, long enough to make studies of equilibrium concentrations possible, is of great interest in many cases but requires very large amounts of radioactivity for large systems.

CONCLUSIONS

The use of the methods reported here yields information concerning:

(1) Residence times and flow patterns in sewage purification plants.
(2) Flow patterns and dilution data in natural systems as rivers, lakes and river mouths.

The methods are important for the localization of suitable sites for new mills and for investigating the feasibility of new or larger waste water discharge systems. The Swedish industry, especially the cellulose industry, is interested in the use of the radioisotope technique for studying water pollution. The same type of investigations will also be of importance in the nuclear power industry in order to study in advance the disposal of radioactive wastes.

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Détection en Continu des Rayonnements β dans les Solvants Aqueux et Organiques

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On décrit un procédé pour la détection en continu et l'enregistrement de la radioactivité dans les liquides sortant de colonnes à chromatographie à l'aide d'un compteur de Geiger-Müller à fenêtre mince. Un dispositif spécial permet d'augmenter l'efficacité du compteur par étalement de la couche liquide. Cette méthode, réalisable avec des appareils d'un type courant, est valable pour des effluents aqueux aussi bien qu'organiques (éther de pétrole, acétone, alcool). Des exemples de séparation de Pm^{147} et de composés marqués au S^{35} et au C^{14} montrent qu'elle est applicable aux activités faibles ou très fortes, aussi bien en chimie préparative qu'en chimie analytique.

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CONTINUOUS DETECTION OF β-RADIATION IN AQUEOUS AND ORGANIC SOLVENTS

A process is described for continuously detecting and recording the radioactivity of liquids emerging from chromatographic columns by means of a thin-window Geiger counter. A special arrangement by which the liquid layer is spread out gives greater counting efficiency. This method, for which standard equipment can be used, is suitable for both aqueous and organic solvents (e.g. petrol ether, acetone, alcohol). Experiments in the separation of Pm^{147} and of compounds labelled with S^{35} and C^{14} show that it is equally suited to low and to very high activity levels, in the fields of both preparative and analytical chemistry.

НЕПРЕРЫВНАЯ ДЕТЕКЦИЯ РАДИАЦИИ В ВОДЯНИСТЫХ И ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ

Описан процесс для непрерывной детекции и записи радиоактивности жидкостей выходящих из хроматических столбов при помощи тонко-оконного счетчика Гейгера. Специальное приспособление, которым жидкий слой простирается, дает возможность лучшего подсчета. Этот метод, для которого может употребляться стандартное оборудование, подходит как к водянистым, так и к органическим растворителям (т.е. керосин, эфир, ацетон, спирт). Опыты отделения Pm^{147} и соединений обозначенных S^{35} и C^{14}, показывают, что это подходит как и для низкого, так и для очень высокого уровня действия в сфере предварительной и аналитической химии.

KONTINUIERLICHE β-MESSUNG IN WÄSSRIGEN UND ORGANISCHEN LÖSUNGSMITTELN

Ein Vorgang zur kontinuierlichen Messung und Registrierung von Aktivitäten in Flüssigkeiten beim Austritt aus chromatographischen Säulen mit Hilfe eines dünnfenstrigen Geiger-Müller-Zählrohres wird beschrieben. Eine besondere Anordnung gestattet die Empfindlichkeit

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† Service des Radioéléments artificiels.

des Zählers durch Ausbreitung der Flüssigkeitschichte zu steigern. Diese Methode, die sich mit den üblichen Apparatetypen durchführen lässt, ist sowohl für wässrige, als auch für organische Eluierungsmittel (Petroläther, Aceton, Alkohol) verwendbar. Beispiele von Pm-147-Abtrennung und von markierten S-35 und C-14-Verbindungen zeigen, dass sie für schwache und für sehr starke Aktivitäten in der präparativen, wie auch in der analythischen Chemie anwendbar ist.

INTRODUCTION

Lors de la séparation de mélanges complexes minéraux aussi bien qu'organiques sur des colonnes de chromatographie, le problème consiste à trouver les fractions où apparaît le produit dont on cherche l'isolement. La solution classique consiste à diviser à l'aide d'un collecteur de fractions l'éluat en un aussi grand nombre de tubes que l'on juge nécessaire, puis à rechercher le composé désiré dans chacun de ces tubes. Avec les produits radioactifs émetteurs de rayonnement β mou (Pm^{147}, C^{14}, S^{35}) on dépose sur goutte prélevée dans chacun des tubes une papier filtre, on évapore le solvent et on mesure la radioactivité sous un compteur de Geiger-Müller.

Différentes solutions ont été proposées pour examiner l'éluat d'une manière continue pour se débarrasser des servitudes d'un travail long et fastidieux. Pour les substances non radioactives, les méthodes sont basées sur les propriétés physiques des solutions sortantes, par exemple le changement de l'indice de réfraction,[1] du pH,[2,3,4] de la conductivité,[5,6,7] de la constante diélectrique,[8] de l'absorption ultra-violette.[9]

La propriété physique caractéristique des radioéléments étant l'émission d'un rayonnement aisément décelable, on pouvait songer à l'utiliser pour analyser en continu les solutions sortantes. En fait, on se heurte à des difficultés provenant de la faible concentration des solutions, de l'absorption des rayons "mous" par le solvant et par la fenêtre du détecteur. Cependant, différents procédés ont été proposés.[10,11,12] Toutes ces méthodes présentent un certain nombre d'inconvénients: faible efficacité, contamination trop facile ou appareillage compliqué.

La méthode que nous décrivons a été utilisée dans nos laboratoires depuis près de deux ans et l'appareillage a été présenté à l'exposition de la Conférence Internationale sur les Radioisotopes dans la Recherche Scientifique (Paris, septembre 1957).

PRINCIPE

Lorsqu'on dépose sur une plaque de verre humide une feuille très mince de polyéthylène-téréphtalate ("Mylar",* "Terphane"†) on constate que cette feuille adhère sur le verre en emprisonnant des bulles d'air. Une fois celles-ci éliminées, on obtient une pellicule d'eau d'une très faible épaisseur. Si l'on pratique maintenant sur la feuille de Mylar un pli parallèle au côté horizontal de la plaque de verre (de façon à ce que la partie du plastique située au-dessus de la pliure ne soit pas en contact avec le verre) (Fig. 1), puis si l'on introduit une goutte d'eau au

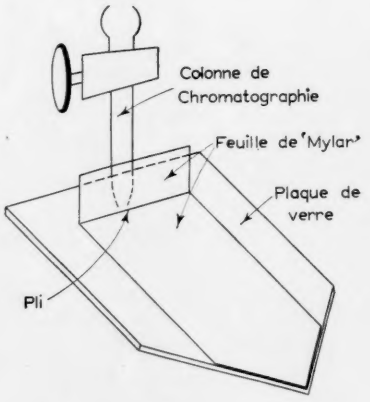

Fig. 1.

* Marque déposée (Du Pont de Nemours).

† Fabriqué sous licence en France par la Société "La Cellophane".

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milieu du pli ainsi défini, on constate que celle-ci disparaît rapidement, qu'elle se disperse sur toute la surface du plastique *sans sortir par les côtés*. Au bout de quelques secondes, elle se rassemble à la partie inférieure et tombe à l'extrêmité effilée ménagée en bas. On réalise ainsi un écoulement lamellaire. L'expérience a montré qu'une goutte d'eau de 50 mg arrive à remplir entièrement une surface de plastique de 25 cm². Si l'on suppose un écoulement régulier, ce qui n'est exact qu'en première approximation, l'épaisseur moyenne de la couche liquide est de 0,02 mm. Le film de téréphtalate n'ayant que 0,002 mm, l'épaisseur totale est encore inférieure au parcours maximum des rayons β mous dans l'eau (0,3 mm).

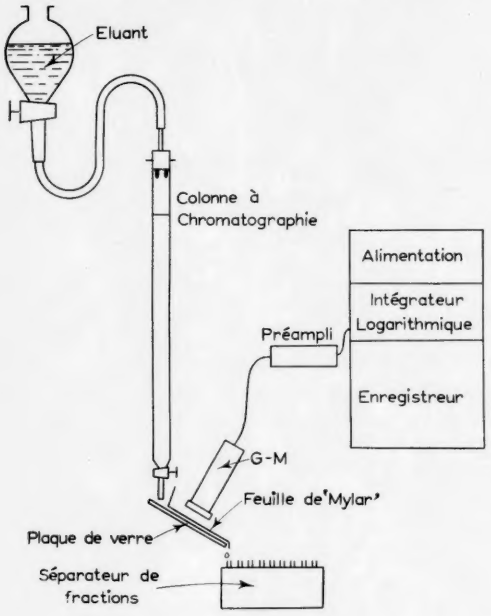

FIG. 2.

Il suffira donc maintenant de placer la pointe effilée de la colonne de chromatographie au milieu du pli, de régler le débit, de placer à 1 mm de l'ensemble plaque-feuille un tube de Geiger-Müller associé avec un intégrateur et un enregistreur (Fig. 2). Toute élévation de la radioactivité dans l'éluat se traduira par un déplacement de l'index de l'enregistreur, et ceci d'une quantité proportionnelle à l'activité reçue.

LIMITE DE SENSIBILITÉ

Pour déterminer la sensibilité de ce procédé, on a fait passer sur une colonne à chromatographie une solution d'un acide organique marqué au C^{14} d'une activité spécifique de 20 μc/mM et on a enregistré l'activité avec un compteur de Geiger ayant une surface de 5 cm², une fenêtre de 1,8 mg/cm², placée à 1 mm du système. Un dosage chimique indique la présence de 0,29 mM (5,8 μc) d'acide dans les tubes correspondants au pic radioactif qui s'est étendu sur 55 cm³ (110 minutes). Une combustion sur le produit isolé ne montre aucun changement dans l'activité spécifique. D'autre part, la surface du pic radioactif tracé sur l'enregistreur, mesurée avec un planimètre de grande précision est de 4.630 mm² (après soustraction du mouvement propre), ce qui représente 1,25 mμc/mm². Cependant, la plus petite activité mesurable se traduit sur le graphique par un pic de 50 mm², ce qui représente l'activité limite, soit 60 mμc en activité totale et 10 mμc/cm³ de solution.

APPAREILLAGE

Les premières expériences ont été réalisées avec un intégrateur linéaire et un enregistreur de 5 mA, 1000 ohms, qui sont des appareils d'un type courant. Cependant, pour avoir une opération entièrement automatique, nous avons été amenés à modifier l'appareillage. Il est composé d'un tube de Geiger, d'un préamplificateur et d'une chaîne comportant une alimentation générale et quatre tiroirs standard: un tiroir d'entrée universel, un tiroir intégrateur logarithmique, un tiroir très haute tension et un tiroir marquage-oscillateur. Le préamplificateur transmet sous basse impédance à

l'amplificateur principal les impulsions provenant du compteur G. M. Après amplification, mise en forme et discrimination, le signal est envoyé dans un circuit de comptage qui fournit une indication proportionnelle au logarithme décimal du taux de comptage et, de là, à un enregistreur potentiométrique de 10 mV gradué en chocs/sec de 0,1 à 10^5. Un système de marquage permet d'indiquer en n'importe quel point du diagramme le changement de tube du séparateur de fractions.*

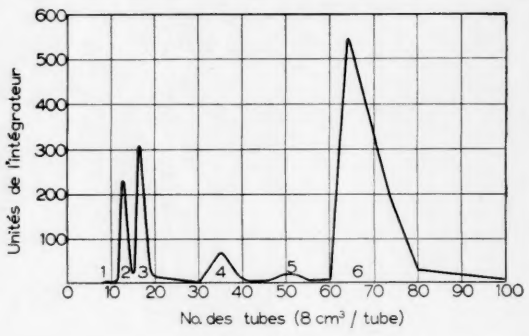

FIG. 3.

EXEMPLES DE SÉPARATIONS

Séparation de la valine-carboxy-C^{14}†

Le produit brut de la réaction entre le cyanure de K–C^{14} (11,5 mc) et l'isobutanal en présence de $ClNH_4$ a été hydrolysé puis passé sur une colonne de résine Dowex 50-X-8. L'enregistrement avec l'intégrateur linéaire a été transcrit sur papier millimétré (Fig. 3). La mesure des surfaces montre que la valine représente 76 pour cent du mélange (3,8 mc) la deuxième impureté 5,3 pour cent, la troisième 10,2 pour cent, la quatrième 7,0 pour cent, la cinquième 1,5 pour cent tandis que le premier pic ne représente que 0,06 pour cent du mélange (environ 3 μc).

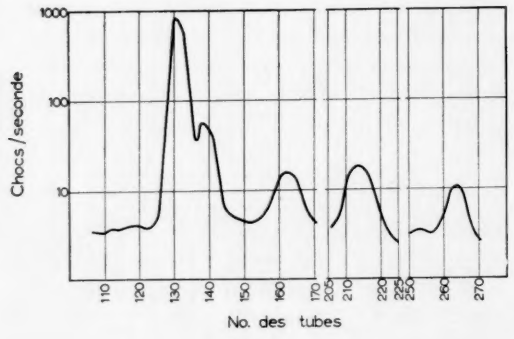

FIG. 4.

Séparation de l'acide glutamique-carboxy-C^{14}† (Fig. 4)

Cet enregistrement a été réalisé avec un intégrateur logarithmique. On voit qu'ici la séparation de l'acide glutamique d'avec l'impureté voisine n'a pas été totale.

Citons parmi les autres séparations effectuées:

— la chromatographie sur Dowex 50 du prométhéum 147, élué avec de l'acide lactique 0,4 M à pH 4; de la méthionine S^{35}, etc.

— la chromatographie sur alumine du produit de la condensation de Réformatsky entre l'acétone-2-C^{14} et le bromacétate d'éthyle en présence d'éther de pétrole[13]. On observe toutefois dans ce cas un gonflement du film plastique.

CONCLUSIONS

En plus d'un gain de temps appréciable et d'une indépendance complète du manipulateur, ce procédé a sur toutes les autres méthodes continues l'avantage de pouvoir s'appliquer non seulement aux solutions aqueuses mais encore à certains milieux organiques (éther de pétrole, acétone, alcool) d'où son application à la chromatographie par adsorption, par partition ou par échange d'ions.

* Nous tenons à remercier M. ROQUEFORT, Service Electronique Industrielle, qui a mis au point et réalisé cet appareillage.

† Nous tenons à remercier MM. PICHAT et AUDINOT pour la communication des résultats expérimentaux.

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Localization of Intracardiac Shunts using Instantaneous Injection of RIHSA with Two-site Sampling*

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Another approach for the localization of left-to-right intracardiac shunts has been described. RIHSA was injected through the tip orifice of a double-lumen catheter as continuous samples of blood were being obtained from the proximal lumen of the catheter and from the brachial artery simultaneously. Radioactive counting rates of the two samples were continuously recorded for calculation by the pip interval method. The catheter sampling sites were selected to demonstrate the specific location at which indicator appeared earlier than at the brachial artery.

Seven of the patients in this study had atrial septal defects. One patient had a ventricular septal defect. Verification of the RIHSA localization of the defect was done in all patients by blood oxygen and pressure studies and in four patients at surgery.

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LA LOCALISATION DE COURT CIRCUIT INTRACARDIAQUE EN EMPLOYANT L'INJECTION INSTANTANEMENT DE RIHSA AVEC ECHANTILONAGE DE DEUX SITES

Il a été décrit une autre façon d'aborder la localisation de communications intracardiaques de gauche à droite. On a injecté RIHSA dans l'orifice de l'extrémité d'un cathéter à deux canaux, tout en obtenant simultanément, des échantillons continus de sang par l'orifice proximal du cathéter et par l'artère brachiale. Par la méthode de "pip interval", on a enregistré sans interruption le compte radioactif des proportions des deux échantillons. Les locations du cathéter ont été choisies pour démontrer l'endroit spécifique où l'indicateur se montre plus vite qu'à l'artère brachiale.

Dans cette étude, sept parmi les patients avaient des défauts septal atrial. La localisation correcte des défauts par les études de RIHSA a été vérifiée par les déterminations d'oxygène dans le sang et par l'étude de la pression chez tous les patients et en chirurgie chez quatre patients.

ОПРЕДЕЛЕНИЕ ЛОКАЛИЗАЦИИ ВНУТРИСЕРДЕЧНЫХ ШУНТОВ С ПОМОЩЬЮ ОДНОВРЕМЕННОГО ЗАБОРА КРОВИ ИЗ ДВУХ МЕСТ ПРИ ВВЕДЕНИИ RIHSA

Описан еще один метод определения локализации шунтов между левым и правым сердцем. RIHSA вводилась в полость сердца через одно из отверстий двухканального катетра, в то время как через другой его канал и одновременно из плечевой артерии

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брались пробы крови. Радиоактивность этих проб непрерывно регистрировалась, чтобы зафиксировать момент появления индикатора в крови, забираемой через катетр и в плечевой артерии. По промежутку времени между появлением индикатора в этих пробах можно судить о состоянии сердечной перегородки в месте расположения катетра.

Описанным методом у семи больных выявлены дефекты перегородки в области предсердий и у одного больного—в области желудочков. Подтверждение найденной с помощью RIHSA локализации дефекта было получено у всех больных путем исследования кровяного давления и кислорода крови, а у четырех больных—и при хирургическом вмешательстве.

LOKALIZATION DER INTRAKARDIALEN KOMMUNIKATION BEI SOFORTIGER INJEKTION DE RIHSA MIT ZWEI-ORTHLICHER BLUTPROBEN UNTERSUCHUNG

Eine andere Methode für die Diagnose der linken zur rechten intrakardialen Kommunikation ist beschrieben worden. RIHSA wurde injiziert durch die Spitzenpore eines doppel Lumenkatheter, wärend laufende Blutproben zur gleichen Zeit von der arteria brachialis und dem proximalen Lumen des Katheters genommenen wurden. Radioactive Errechunngen der beiden Blutproben wurden laufend registriert für Kalkukationen bei der piep intervall Methode. Die Katheter Blutprobenörter wurden so erwählt un zu demonstrieren, wo der Indikateur früher erscheine, denn in der arteria brachialis.

Sieben der patienten hatten ein atriales Septumdefekt in diesen Untersuchungen. Korreckte Localization der Defekte mit RIHSA Untersuchung wurden mit Blutoxigen und Pressions Determinationen in allen Patienten bestätigt und in vier Patienten wärend der Herzoperation.

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INTRODUCTION

In 1950 Friedlich[1] presented a dye dilution curve of a patient with Eisenmenger's complex demonstrating an intracardiac shunt by the curve. The Mayo group[2–7] has reported extensive observations using instantaneous injections of T-1824 in the study of right-to-left and left-to-right intracardiac shunts. They showed that right-to-left shunts could be localized by properly positioning the catheter tip in relation to the shunt. A right-to-left shunt caused a peak on the build-up portion of the arterial concentration curve resulting in a double peaked curve when the indicator was injected at the level of the defect. Left-to-right shunts were detected by noting evidence of early recirculation causing distortion of the downslope of the arterial concentration curve. We[8] have obtained similar curve distortions in shunts using radioactive iodinated human serum albumin.

Braunwald *et al.*[9] have reported arterial dye dilution curves showing that they were able to localize left-to-right shunts by injecting the indicator into selected sites at left heart catheterization. We report studies on the localization of left-to-right shunts at right heart catheterization by the injection method utilizing two sampling sites simultaneously. In a recent report Fox *et al.*[10] indicate that this technique would be valuable in detecting small left-to-right cardiac shunts.

METHOD

A detailed description of the apparatus has been reported elsewhere.[11] A double-lumen catheter was used at cardiac catheterization for this study. The indicator was injected through the distal (tip) orifice and a continuous blood sample was obtained through the proximal orifice. The initial injection and sampling site within the heart was selected to demonstrate best the clinically suspected lesion. A subsequent injection was

sometimes necessary to complete the localization of the lesion.

During the test a blood sample from a brachial artery was drawn continuously at a flow rate of 40 ml/min through polyvinyl tubing (i.d. 2·1 mm) looped in a well crystal. The sample from the proximal orifice of the catheter was drawn similarly through a tube of smaller diameter looped in another well crystal. The smaller tubing for the catheter sample contained about half as much volume within the counting geometry. The sampling rate from the catheter was held constant at 18 ml/min, air being excluded from the system.

The constant-sampling-rate to counting-geometry-volume ratio was kept about 4·8 for the two systems. We found, on testing the two systems, that when square wave changes in indicator concentration were introduced into the tubing system used for the arterial sample that it required 1·3 sec for the counting rate to go from 2 per cent to 90 per cent of the peak (static) counting rate of the indicator. When a similar study was done on the catheter sampling system (including the catheter) with the 4·8 sampling rate to counting geometry ratio, we found that it required 5·3 sec for the counting rate to go from 2 per cent to 90 per cent of the peak counting rate of the indicator.[12]

When the test was run, 2 ml of RIHSA solution at a concentration to give about 1·0 μc/kg was injected through the distal orifice of the catheter by an injection pipette[13] with a 10 ml saline flush. The exact time of injection was recorded on the tracing. The counting rate of each well crystal scaler was recorded continuously on two channels of a recording oscillograph* by the pip interval method.[14]

The location of the catheter injection site and sampling site was determined by direct fluoroscopy and pressure recordings before and after the test. If a repeat was needed to localize the defect further, the catheter was repositioned as suggested from the data at hand. Practically all defects could be demonstrated and localized with one or two injections.

Immediately after the last patient determination a 1 : 1000 dilution of the indicator was counted in the tubings of the respective well crystals. Carrier albumin was used in the preparation of this standard dilution.

The time required for the sample to pass from the tip of the needle in the brachial artery and from the proximal orifice of the double-lumen catheter to the respective well crystals was subtracted from the time of injection. One further adjustment was made on the catheter sample concentration values before plotting. To compensate for the difference of the counting efficiencies of the two assemblies, the concentrations of the catheter sample at each second were multiplied by the ratio of the net counting rates of the standard dilutions in the respective well crystals. The concentrations were then graphed on semilogarithmic paper. The resulting second-by-second plot of the two curves could be compared directly showing the concentrations as they appeared at the catheter tip and brachial artery sampling sites. Where possible, flow rate calculations were performed by accepted formulas. Table 1 presents the subjects studied to date and their diagnoses.

RESULTS

We have reported elsewhere[11] that in a group of 15 patients without shunts the indicator first appeared from 0 to 11 sec (average 4·4 sec) later at the right ventricle and reached peak concentration from 5 to 20 sec (average 12·3 sec) later at the right ventricle than at the brachial artery following an injection of RIHSA in the main pulmonary artery. In the 10 patients presented with left-to-right shunts the indicator appeared from 1 to 7 sec (average 2·2 sec) earlier in the catheter sample and reached peak concentration from 1 to 5 sec (average 3·0 sec) before the main peak concentration in the brachial artery sample occurred.

* Polyviso Recorder, Sanborn Instrument Company, Cambridge, Massachusetts.

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TABLE 1. Patients at catheterization with two-site sampling

Patient	Sex	Age (yr)	Ht. (cm)	Wt. (kg)	Diagnosis from clinical and catheterization data	Diagnosis from two-site sampling method
K. T.	M	28	170	67	Atrial septal defect	L–R Shunt at RA
P. S.	M	34	164	70	Atrial septal defect	L–R Shunt at RA
R. P.	M	35	183	87	Small patent ductus arteriosus	L–R Shunt at MPA
C. H.	F	31	160	47	Atrial septal defect	L–R Shunt at RA
G. M.	F	37	160	48	Atrial septal defect	L–R Shunt at RA
R. B.	F	36	164	88	Atrial septal defect	L–R Shunt at RA
S. W.	M	39	167	66	Atrial septal defect	L–R Shunt at RA
N. H.	M	17	148	52	Ebstein's Disease	L–R and R–L Shunt at RA
S. A.	F	15	136	52	Ventricular septal defect	L–R and R–L Shunt at RV
A. B.	F	36	155	57	Atrial septal defect	L–R Shunt at RA

All the patients included in this study had unquestioned shunts at the reported sites as demonstrated by cardiac catheterization and clinical findings. In addition, patients C. H., R. B., and S. W. were found to have atrial septal defects at surgery, and in patients N. H. and G. M. the catheter was passed through the atrial septal defects.

Three patients are presented to illustrate the findings by this technique.

S. W. was a 39-year old male who had a known congenital heart defect since five

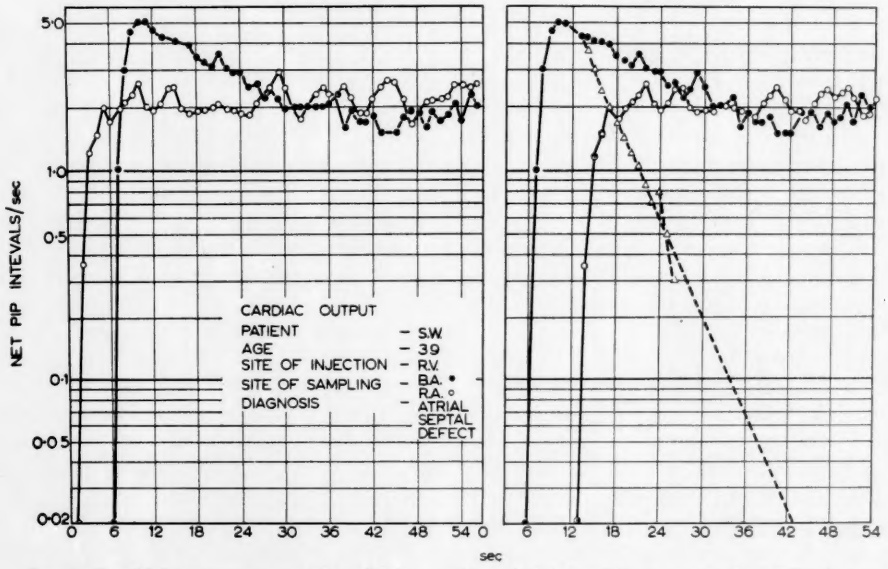

FIG. 1. Brachial artery concentrations (higher peak) and right auricle concentrations following an injection of RIHSA (1·0 μc/kg) into the right ventricle. The left hand portion shows the concentrations as they occurred at the respective sampling sites. The right hand portion shows the concentrations with the curve of catheter sample shifted to compensate for transit time from right auricle to brachial artery. Triangles are values obtained by subtracting RA values from BA values at corresponding times. Net counts per second can be obtained for this curve by multiplying the net pip intervals per second by 64 (the scaler setting).

years of age. No cyanosis was present. At cardiac catheterization the oxygen–hemoglobin saturation was 65 per cent in the superior and inferior venae cavae and increased to 90 per cent in the right auricle near the tricuspid valve. The pressures were 8/3 mm Hg in the right auricle and 35/3 mm Hg in the right ventricle.

The first injection of RIHSA was made into the right ventricle with catheter sampling from the right atrium. Fig. 1 shows the results obtained from this injection. The left hand portion of the figure shows the concentrations as they occurred at the brachial artery and right atrium. The brachial artery curve exhibits evidence of a considerable left-to-right shunt which produced a marked distortion with almost complete absence of the downslope. The right auricle sample shows that there is a considerable quantity of indicator at the right auricle before it begins to appear at the brachial artery. This indicates a left-to-right shunt at the atrial level.

No flow rate calculations can be made from the brachial artery curve unless one uses the appearance time method of Dow,[15] or forward triangle method of Ramirez De Arellano.[16] Since the catheter sample gives a fairly close approximation of the concentrations of the interfering recirculation indicator at each second, the downslope can be approximated by subtracting the catheter sample concentrations from the brachial artery sample concentrations. Before this is done, however, the right atrial sample concentrations must be shifted to compensate for the transit time from right atrium to brachial artery. This transit time we[11] have shown to be essentially equal to the peak concentration time. The right hand portion of the slide shows the downslope, indicated by triangles of the brachial artery sample that was obtained in this patient when the catheter sample concentrations were shifted to the right to compensate for the transit time and subtracted at each second from the brachial artery sample concentrations. The flow rate calculated from the curve thus obtained was 11 l/min.

In this patient another catheter was next inserted via a femoral vein and went through the atrial septal defect. An injection was then made through this catheter directly into the left ventricle with the sampling catheter orifice in the right ventricle.

Fig. 2 shows the concentration curves obtained at the brachial artery and right ventricle simultaneously following this injection. The brachial artery curve was not distorted by shunting, and the downslope has a marked percentage drop before recirculation occurs. The recirculation curve continues to rise until about 42 sec after injection because the indicator must traverse the varied length channels from the left ventricle to the right atrium and pulmonary circuit. The right ventricular sample shows that the indicator appeared 5 sec later at the right ventricle than at the brachial artery signifying that there was no left-to-right shunt between the two ventricles. Combining the data of the two injections we know that there is a defect between the auricles but none between the ventricles. An atrial septal defect was found and closed at surgery.

N. H. was a 17-year old white male who was born a "blue baby" and had had exertional dyspnea all his life. Cyanosis and clubbing of fingers and toes was present. At catheterization there was no significant increase in oxygen content from the superior and inferior venae cavae values to the pulmonary arteries with the oxygen–hemoglobin saturation ranging between 67 and 72 per cent. The brachial artery oxygen–hemoglobin saturation was 91 per cent while breathing 100 per cent oxygen. The right auricle pressure was 7/2 mm Hg, and the right ventricle pressure was 16/3 mm Hg.

The first injection of RIHSA was made into the right auricle with sampling from the superior vena cava and brachial artery. The brachial artery curve showed a double peaked curve typical of a right-to-left shunt. The catheter sample showed that the indicator appeared 3 sec later and reached a peak 3 sec later at the superior vena cava than at the brachial artery.

An injection was then made into the right ventricle with sampling from the right

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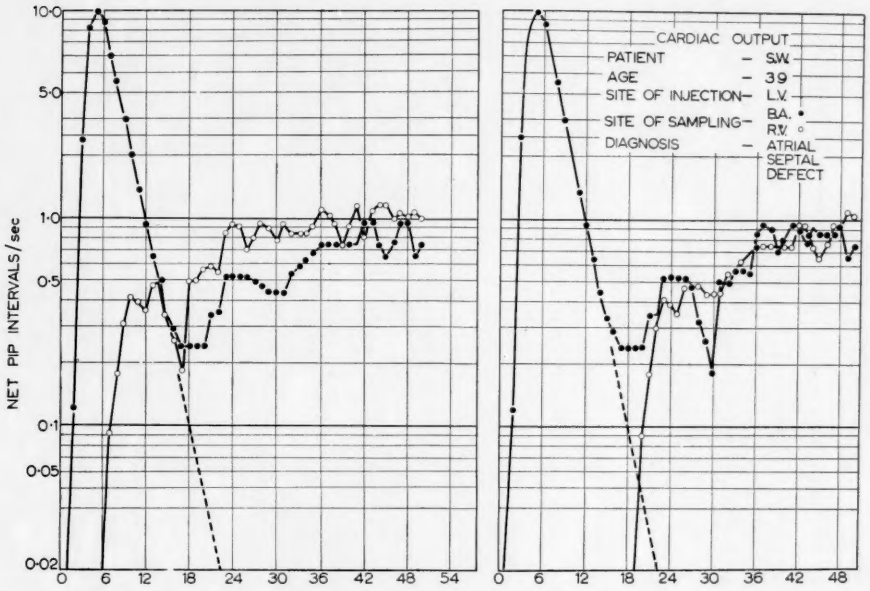

FIG. 2. Brachial artery concentrations (higher peak) and right ventricle concentrations following an injection of RIHSA (1·0 μc/kg) into the left ventricle. The left hand portion shows the concentrations as they occurred at the respective sampling sites. The right hand portion shows the concentrations with the catheter sample concentration curve shifted to the right to compensate for transit time from right ventricle to brachial artery. Scaler setting was 64 (see caption to Fig. 1).

auricle and brachial artery. The brachial artery curve had a normal shape except for early appearance of recirculating indicator. The right auricle sample showed that the indicator appeared 7 sec earlier and reached a peak 5 sec earlier at the right auricle than at the brachial artery.

The results of the two injections in this case allow the conclusion that the patient has a right-to-left and left-to-right shunt between the auricles. The defect between the auricles was further demonstrated when the catheter was passed through the atrial septal defect.

S. A. was a 15-year old female with a congenital heart defect known since the age of two. At catheterization the oxygen–hemoglobin saturation ranged between 59 and 63 per cent in the venae cavae and right ventricle. The pressures were normal in the right auricle and 100/4 mm Hg in the right ventricle with a brachial artery pressure of 110/75 mm Hg.

The first injection was made in the main pulmonary artery with catheter sampling proximally from the right ventricle. The left hand portion of Fig. 3 shows the results of this injection. The brachial artery curve has a distorted downslope due to a left-to-right shunt. The catheter sample shows recirculating indicator at the right ventricle before the initial circulating indicator appeared at the brachial artery.

The second injection was made into the right ventricle with catheter sampling from the right auricle. The right hand portion of Fig. 3 shows the result of this injection. The brachial artery curve has a double peak due to a right-to-left shunt and distortion of the downslope due to early recirculating indicator from a left-to-right shunt. The right auricle curve when compared with the brachial artery curve shows that the indicator appeared later and reached a peak later at the right auricle than at the artery.

The results of these two injections in this

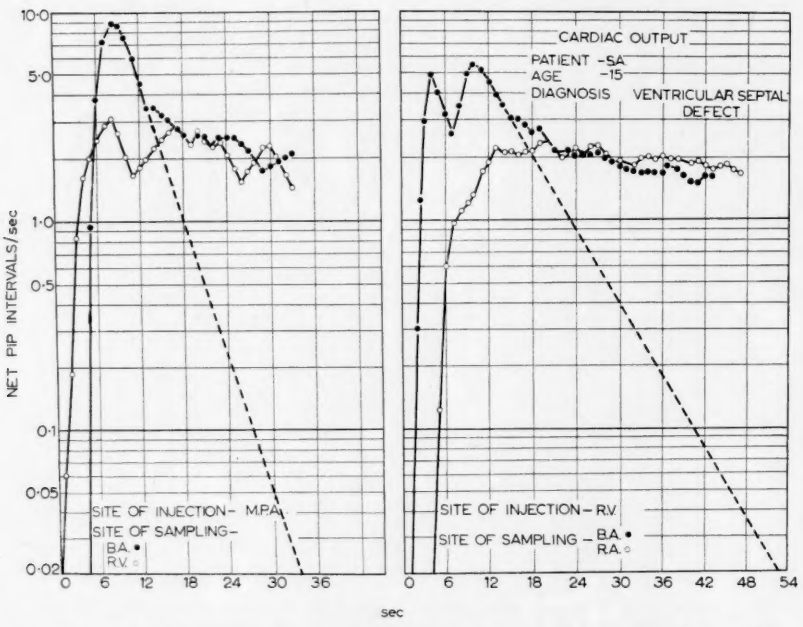

FIG. 3. Brachial artery (higher peaks) and catheter sample concentrations as they actually occurred. The left hand portion shows the two curves obtained following an injection into the M.P.A. The right hand portion shows the two curves obtained following an injection into the right ventricle. Each injection of RIHSA was 1·0 μc/kg of body weight. Scaler setting was 64 (see caption to Fig. 1).

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case show that there is a right-to-left and a left-to-right shunt between the ventricles, but that there is no left-to-right shunt between the auricles.

DISCUSSION

The localization of intracardiac shunts is classically done by following the changes in oxygen content or oxygen–hemoglobin saturation and pressure changes in the right heart and pulmonary artery. Even in the best of hands these methods may give equivocal results in some cases. Indicator curves may give considerable assistance in the localization of shunts. Right-to-left shunts can be detected and located by selection of injection site in right heart. Using the method we have described, left-to-right shunts can also be detected and localized. This can be accomplished if the indicator is injected just beyond the sampling site and the sampling site is selected within the heart or pulmonary artery to demonstrate the location at which shunted indicator appears in significant quantity earlier than that recirculating from the systemic circulation.

The injection method for shunt localization and blood flow rate determinations has certain advantages. Indicators can be selected to give quite accurate results. Blood flow rates can be measured even in some cases with shunts. The presence or absence of more than one intracardiac defect can be shown as in the case of S. W. This is quite important to know since the treatment for a combined atrial and ventricular defect would be different than for either of the defects alone. Further study is being given to the simultaneous catheter and arterial concentrations to determine whether shunt flow rates can be calculated in the presence of a high percentage shunt. Dow[14] and

RAMIREZ[15] have presented formulas for the estimation of cardiac output in patients with left-to-right shunts using the first portion of the arterial concentration curve to the peak concentration. At the present time we have insufficient data on pulmonary flow by our method for comparison with their methods.

Sampling from the catheter has presented the greatest difficulty in the two-site sampling technique. Several conditions must be met. The flow rate of the sample of blood within the counting geometry of the well crystal should be sufficient to reflect properly the changing concentrations of the indicator. The volume of the sample within the counting geometry must be large enough to allow a statistically significant counting rate on the tracer, and the dose of radioactive tracer must be kept as low as possible. The objective, then, is to obtain a compromise between counting volume, sampling flow rate, and a safe, yet adequate, counting rate of the tracer.

As the radius of the catheter and tubing within the well is decreased, the resistance increases by a function of the radius to the fourth power. This increased resistance limits the sampling rate by suction and also produces streaming of the blood so that the central portion of the stream is moved along rapidly and the peripheral portion lags behind. This is the main factor which limits the response time of the system as we are using it. The recording system has essentially a 0·1 sec response time at 10 pip intervals per second. The sampling system and counting geometry account for the remaining portion of the 1·3 sec for the brachial artery and 5·3 sec for the catheter sample 90 per cent response times.[cf 12]

The volume of the system from catheter opening to well crystal together with the sampling rate determine the amount of correction time needed for the time base so that the graph reflects concentration changes as though the well crystal were at the catheter opening. A few tenths of a second error in this measurement has not been found to be significant in the adult, but duration of events in the circulation of a child are much shorter, and closer tolerance would be needed for correct interpretation. The sampling rate must be regulated with known precision.

This study has been limited to adults and adolescents. Radioactive isotopes lend themselves very well as indicators for this type of study, but smaller radiation doses than can be attained by RIHSA will be advisable in children. We have found that I-131-labelled Diodrast gives flow rate and central volume dilution values practically identical with those of RIHSA in the initial transit through the lungs. Apparently it does not transude through the pulmonary capillaries in the initial transit through the lung. If the blood samples and standard dilutions of the injected material are both counted in the same geometry, there is no need for a 10 min equilibrium sample which would result in an error in the cardiac output because Diodrast is rapidly lost from the vascular bed. The use of Diodrast for the localization of intracardiac shunts would have the advantage over RIHSA of a lower radiation dose to the patient and a much lower background for repeat tests. A report of a comparison of these two indicators for shunt localization is in preparation. At present the radioisotope recording–detecting system has an advantage over the dye detecting–recording system because of the shorter response time possible with the radioisotope system.

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The Determination of Gallium and Molybdenum in Biological Material by Activation Analysis

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Methods are described for the determination of gallium and molybdenum in biological material using the technique of activation analysis. The limits of detection are 3×10^{-10} g for gallium and 10^{-7} g for molybdenum. The method has been used to determine these elements in tomato seeds and in whole blood. Tomato seeds normally contain about 0·01 p.p.m. of gallium and 1–3 p.p.m. of molybdenum, but the latter element can be reduced by at least 95 per cent by growing the plants under conditions of molybdenum deficiency. 100 ml of blood contains about 0·05 μg of gallium and 1·4 μg of molybdenum.

LE DOSAGE DU GALLIUM ET DU MOLYBDÈNE DANS LE MATÉRIEL BIOLOGIQUE AU MOYEN DE L'ANALYSE À ACTIVATION

Des méthodes sont décrites pour le dosage du gallium et du molybdène dans le matériel biologique, employant la technique de l'analyse à activation. Les limites de dosage sont 3×10^{-10} g pour le gallium et 10^{-7} g pour le molybdène. La méthode a servi au dosage de ces éléments dans les graines de tomate et dans le sang entier. Les graines de tomate contiennent ordinairement environ 0,01 p.p.m. de gallium et 1–3 p.p.m. de molybdène, mais ce dernier élément peut se diminuer de 95 pour cent au moins si on fait pousser les plantes sous des conditions de manque de molybdène. 100 ml de sang contient environ 0,05 μg de gallium et 1,4 μg de molybdène.

ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ ГАЛЛИЯ И МОЛИБДЕНА В БИОЛОГИЧЕСКИХ О ЪЕКТАХ МЕТОДОМ АКТИВАЦИОННОГО АНАЛИЗА

Описаны методы определения содержания галлия и молибдена в биологических объектах с помощью техники активационного анализа. Порог чувствительности составляет 3×10^{-10} г для галлия и 10^{-7} г для молибдена. Метод применен для определения содержания этих элементов в семенах томатов и в цельной крови. Семена томатов обычно содержат 0,001% галлия и 0,1–0,3% молибдена. Количество последнего может быть, однако, уменьшено по крайней мере на 95% путем выращивания растений в условиях молибденовой недостаточности. В 100 мл крови содержится около 0,05 μг галлия и 1,4 μг молибдена.

DIE BESTIMMUNG VON GALLIUM UND MOLYBDEN IN BIOLOGISCHER MATERIE MIT HILFE DER AKTIVIERUNGSANALYSE

Methoden zur Bestimmung von Gallium und Molybden in biologischer Materie mit Hilfe der Methode der Aktivierungsanalyse werden beschrieben. Die Nachweisgranze für Molybden beträgt $3 . 10^{-10}$ g Die Methode wurde zum Nachweis dieser Elemente in Samen von Tomatenpflanzen und in Blutproben verwendet. Normale Tomatensamen enthalten etwa 10^{-8} g Ga/g Substanz und etwa bis $3–10^{-6}$ g Mo/g Substanz, wobei für letzteres eine Abnahme von mindestens 95% erzeilt werden kann, wenn die Pflanzen unter Molybdenmangelbedingungen aufgezogen werden. 100 ccm Blut enthalten etwa 00,5 μg Ga und 1,4 μg Mo.

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INTRODUCTION

MOLYBDENUM is an essential element in both animals and plants, where it has been shown to be an essential constituent of xanthine oxidase[1] and nitrate reductase[2] respectively. It is frequently present in extremely minute quantities where the colorimetric technique described by STANFIELD[3] is inapplicable. However, very sensitive microbiological techniques have been described for this element.[4] Gallium is not believed to be essential, since claims by STEINBERG[5] that it was a necessary element for *Aspergillus niger* and *Lemna minor* were later retracted by the same author.[6] There are no methods for determining submicrogram quantities of gallium in biological material described in the literature.

It was required to determine molybdenum in small samples of seed, and the method of neutron activation described below was evolved for this purpose. Molybdenum is readily separated from most other elements by solvent extraction with ether from 6 N hydrochloric acid, as is the case with gallium. Although gallium is generally present in far smaller quantities than molybdenum, it is much more strongly activated by thermal neutrons, so that it is necessary to remove it from the radioactive molybdenum by further chemical steps. These steps led to the production of radiochemically pure gallium which could be determined incidentally to the molybdenum analysis.

Radioactivation analysis for molybdenum has been briefly described by several workers in the field of metallurgy.[7,8,9] Radioactivation for gallium has been much more widely used, probably because of the lack of other analytical methods for this element, following the pioneering studies of BROWN and GOLDBERG.[10] Later work is listed in a recent bibliography.[11] Table 1 lists the radioisotopes of gallium and molybdenum produced by neutron activation: Ga^{72} and Mo^{99} were the isotopes used in the present work.

TABLE 1. Gallium and molybdenum radioisotopes produced by neutron activation (Activated for 12 hr in a flux of 10^{12} neutrons/cm²/sec)

Isotope	Half-life	mc/g produced	mc/g after 7 hr decay
Ga^{70}	21 min	260	0·0003
Ga^{72}	14 hr	140	100
Mo^{93}	6·9 hr	0·12	0·06
Mo^{99}	2·8 days	0·62	0·58
Mo^{101}	15 min	3·1	0·0000

EXPERIMENTAL

For gallium, the best conditions are activation for 14 hr followed by 4 hr decay, while for molybdenum one should use a 3 day activation period followed by 3 days decay. In practice, the samples were activated for periods between 12 hr and 3 days and allowed to decay for at least 6 hr before counting.

The tomato seeds were collected with the minimum of contamination as described by BOWEN.[12] At least 0·3 g (100 seeds) were needed for analysis. 5 g blood samples were withdrawn using a carefully cleaned hypodermic syringe and immediately ejected into clean polythene ampoules. The samples were packed, together with standards of 20 μg spec. pure molybdenum and 1 μg spec. pure gallium, in a polythene bag inside an aluminium can. The can was then irradiated in the Harwell Pile BEPO in a flux of about 10^{12} thermal neutrons/cm²/sec. After irradiation, the biological material was dissolved in hot fuming nitric acid, with a few drops of perchloric acid in the case of the blood samples. 10 mg of molybdenum carrier (as ammonium molybdate) and 5 mg of gallium carrier (as the nitrate) were added, together with holdback carriers of copper, cobalt, manganese, phosphorus and yttrium. The solution was evaporated to about 1 ml and then made up to 10 ml and 6 N in hydrochloric acid. It was transferred to a 50 ml

separating funnel and shaken with an equal volume of ether, the aqueous layer discarded and the ether washed twice with 6 N hydrochloric acid. The ether layer was then extracted twice with 5 ml of water, and the aqueous layers combined and boiled to evaporate traces of ether. The aqueous fraction was then made 2 N in hydrochloric acid and molybdenum sulphide was precipitated by adding ammonium sulphide. This was centrifuged down and a few drops of 10% copper sulphate were added to scavenge any molybdenum not precipitated in the first stage. The supernatant from this procedure was worked up for gallium by boiling out H_2S and then making alkaline with potash and scavenging 3–4 times with ferric hydroxide. The gallium remaining in solution was precipitated as the 8-hydroxy quinolate in an ammonium acetate buffer at pH 6. The precipitate was soluble in acetone, so it was washed three times with water slurried on to an aluminium counting tray, weighed to determine the chemical yield and counted with an end-window Geiger counter.

The molybdenum sulphide was washed with 2 N HCl, and then dissolved in a little hot fuming nitric acid. The acid was neutralized with potash and the solution scavenged with ferric hydroxide. The supernatant was made 3 N in nitric acid and excess α-benzoin oxime was added to precipitate the molybdenum. Two further cycles of scavenging and α-benzoin oxime precipitation were employed, largely to remove traces of phosphorus-32, and the final molybdenum α-benzoin oximate was thoroughly washed with water and acetone before plating, weighing and counting as before.

The whole procedure took about 4 hr for eight samples. Losses of each element were tested using dummy runs, and chemical yields were of the order of 50–70 per cent. The gallium samples were often contaminated with long lived impurity which was found to have a 14 day half-life and was almost certainly phosphorus-32, but contamination of the molybdenum samples was much rarer.

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RESULTS

Table 2 shows where the losses occur in the chemical steps, from a replicated dummy run.

TABLE 2. Losses in chemical steps

Chemical step	% Mo lost	% Ga lost
Et_2O extraction of 6 N HCl	12·4	2·6
MoS precipitation	1·7	1·4
$Fe(OH)_3$ scavenge	5·0	2·2
Ga oxinate precipitation	—	0·1
Mo α-benzoin oximate precipitation	5·1	—
Total	24·2	6·3

Self absorption curves were constructed for both elements and it was found that small corrections were necessary for self absorption in molybdenum α-benzoin oxime precipitates exceeding 0·03 g in weight. No such correction was found to be needed for gallium-72. This is presumably because the β-rays from gallium-72 have a much greater energy than those from molybdenum-99.

It was originally intended to weigh the molybdenum as silver or lead molybdate which is standard practice, but this involves destruction of the α-benzoin oxime with perchloric acid and it was hoped that this could be avoided. In fact consistent results were obtained on precipitating 4–20 mg amounts of molybdenum and weighing as the α-benzoin oxime compound. Thus six aliquots of ammonium molybdate each containing 4 mg of Mo gave a mean weight of α-benzoin oxime precipitate of 0·0231 ± 0·00045 g (theoretical 0·0232 g). In the same way the consistency of weighing gallium as the 8-hydroxy quinolate was tested and found to be satisfactory.

Recovery of 10 μg aliquots of molybdenum and 5 mμg aliquots of gallium added to tomato seeds was also tested and found to be good.

TABLE 3. Molybdenum and gallium content of biological material

Materials	μg/g Mo	μg/g Ga	No. of replicates
Tomato seeds (grown on Analar chemicals + Mo)	1·90	0·014	10
Tomato seeds (grown on Analar chemicals − Mo)	0·21	0·013	12
Tomato seeds (grown on purified chemicals + Mo)	2·50	0·0077	3
Tomato seeds (grown on purified chemicals − Mo)	0·09	0·0030	3
Whole blood from rat	0·014	0·00055	4

Table 3 shows results which were obtained with the biological material studied. The tomato plants were of the variety Moneymaker, grown in sand culture on Analar chemicals some of which were purified according to the directions given by HEWITT.[13] Control plants were supplied with molybdenum and gallium at the rate of 0·019 p.p.m. and 0·005 p.p.m. respectively in the nutrient solution: added molybdenum was omitted from the solution for watering the deficient plants. The Birmingham strain of Wistar rats was used for blood samples.

DISCUSSION

There are a number of possible sources of error in the method which should be mentioned. The neutron flux used was consistent to ±2 per cent over the contents of the can, and statistical counting errors were kept as low as possible. Gallium-72 is produced by a number of nuclear reactions other than $Ga^{71}(n, \gamma)$, for example $Ge^{72}(n, p)$, $Ge^{73}(\gamma, p)$, $As^{75}(n, \alpha)$ and $U^{235}(n, f)$. The cross sections of all these reactions are likely to be low, however, as are the amounts of these interfering elements in ordinary biological material. In the same way molybdenum-99 could be produced by the $Ru^{102}(n, \alpha)$ and $U^{235}(n, f)$ reactions, and while the first is likely to be of negligible importance the second reaction could interfere with the analysis of samples of relatively high uranium content, since the fission yield of Mo^{99} is 6·1 per cent. The uranium content of blood is 0·015 μg/g according to NEUMAN,[14] and slow neutron fission of the U^{235} in this will give rise to Mo^{99} corresponding to approximately 0·001 μg/g molybdenum in the original sample. Since the uranium content of the tomato seeds used was not known, it was investigated by activating six replicate portions of 100 seeds for 12 hr and measuring how much barium-140 was produced by fission of the uranium-235 originally present.[15] After activation the seeds were dissolved in 80% nitric acid and 20 mg of barium carrier were added. The barium nitrate precipitate was centrifuged off, dissolved in water and reprecipitated twice more with 80% nitric acid. It was dissolved in dilute ammonia and the solution was scavenged with ferric hydroxide. Finally the barium was precipitated as the chromate in an ammonium acetate/acetic acid buffer at pH 6·0. Fourteen days after activation there were no detectable counts on any of the barium chromate fractions, indicating that there was too little uranium in the seeds to give rise to spurious molybdenum activity.

Equilibration between the activated isotopes and added carrier was probably good. Test tube experiments showed that the coloured products obtained by reducing molybdates with zinc and hydrochloric acids were instantaneously oxidized back to the molybdate with fuming nitric acid. Gallium has only one valency state, so it is unlikely to give trouble in this way. The ethereal extraction should remove all elements except Au^{III}, Fe^{III}, In^{I}, P, Sb^{V} and Tl[16]. Gold, antimony and some thallium should co-precipitate with molybdenum sulphide and be washed away from the

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α-benzoin oxime precipitate. Active iron and phosphorus are removed by the ferric hydroxide scavenging procedure, so that the most likely impurities in the gallium fraction would appear to be indium and thallium. Both these elements are much less abundant than gallium, and produce isotopes of very different half-life on activation. Despite the high neutron cross section for indium, no 54 min activity which might be due to In^{116} was observed in any gallium precipitate.

In counting molybdenum-99, it was found advisable to allow the samples to decay for one half-life (67 hr) after activation, as this allows the short lived molybdenum-93 to decay completely and ensures that the Mo^{99} is in equilibrium with its radioactive daughter product, (Tc^{99m}).

The tomato seed results show that it is possible to reduce the molybdenum content of seeds by 90 per cent by growing plants on nutrient solutions deficient in molybdenum, and by 95 per cent if the chemicals used are specially purified. The gallium results show that the purification technique used removed at least 50 per cent of the gallium for Analar chemicals, though it was designed to remove traces of molybdenum and other elements essential for plant growth. There seem to be few, if any, comparable data for seeds in the literature. CANDELA and HEWITT[17] have shown that tomato stem and leaf tissue contain from 0·11 to 2·6 μg/g molybdenum in normal plants and from 0·005 to 0·07 μg/g in deficient plants: while their figures agree in order of magnitude with mine, these authors appear to have produced more severe deficiency than I could obtain. Molybdenum has seldom been determined in blood and the only published figures appear to be those of TER MEULEN[18] and DICK and BINGLEY[19] who found 0·03–0·14 and 0·005–0·01 μg/g respectively.

STITCH[20] could not detect molybdenum in ashed blood using arc spectrography which was sensitive to 0·2 μg/g. Gallium has not previously been sought in blood.

The content of these elements in blood is so low that the amounts found may well be in error by reason of contamination before activation. Since about 5 ml of blood was needed for each analysis, this was extracted with a hypodermic syringe with a stainless steel needle. The molybdenum content of this particular steel was not determined, but steels can contain up to 2·5 per cent of molybdenum, which might be a source of contamination. However, 5 ml replicate samples of quartz distilled water discharged from the same syringe were not found to be contaminated with molybdenum when they were analysed by this method. Even with 5 ml of blood the resources of the activation method were strained to the limit to detect molybdenum, and it is to be hoped that other analytical methods will be brought to bear on this problem.

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technical notes

Isotopic Analysis of Oxygen in Inorganic Compounds

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A semimicro method has been developed for analysing the isotopic composition of various inorganic compounds, including oxides, anions and water. The samples are heated to 400°C with a mixture of mercuric chloride and mercuric cyanide; the carbon dioxide formed is purified for analysis over zinc amalgam at 200°C.

THE isotopic composition of oxygen in inorganic compounds was determined by various methods. These methods have been reviewed eleswhere[1] and need not to be presented here in detail. The only method covering an extensive range of compounds is the one using fluorine compounds as reagents, preferably $KBrF_4$ or BrF_2SbF_6.[2] This method is rather elaborate and requires equipment and reaction vessels made of oxygen-free materials. In the field of organic compounds, an elegant method of analysis[3] using mercury chloride as reagent and analysing the carbon dioxide formed, was developed; the hydrogen chloride formed as by-product is eliminated in this procedure by reaction with 5,6-benzoquinoline. We have modified and extended this method to include a whole range of inorganic compounds.

In our procedure, we use mercuric cyanide in addition to mercuric chloride, in order to provide carbon atoms for the formation of carbon dioxide.* Gaseous cyanogen is formed as a by-product in this procedure and in analysing water or other hydrogen-containing compounds, hydrogen chloride is formed as well. Both of these by-products are separated from the carbon dioxide by reaction with zinc amalgam at 200°C. Zinc is reactive enough to form a cyanide, and on the other hand zinc cyanide has a temperature of decomposition high enough to allow a quantitative conversion of cyanogen to zinc cyanide under our conditions.[4] Hydrogen chloride reacts obviously with zinc forming zinc chloride and hydrogen, which may be easily separated from the carbon dioxide. On the other hand, there is no interaction between zinc amalgam and carbon dioxide at the given temperature.

Our method of obtaining carbon dioxide from inorganic oxygen-containing materials gave positive results with a whole range of compounds including the oxides of iron, cobalt, copper, zinc, lead, mercury, boron, barium, uranium, silver and manganese (the only oxides that failed this procedure, were aluminum and chromium sesquioxides). Next we succeeded in analysing phosphates, sulphates and arsenates as their barium salts and the lithium and potassium salts of nitrous and nitric acids; on the other hand, dry silicates failed to give off any carbon dioxide. This last fact is of practical importance, as it enables the reaction to be carried out in glass vessels without risk of isotope dilution. In addition to the above mentioned compounds, our method has been adapted to water analysis. Using our method, it became possible to analyse water samples of 2–5 mg.[5]

It seems, that all elements having a lower free energy of formation of their chloride derivatives as compared to their oxides, will yield carbon dioxide by our method. In addition to these, there are elements like iron, uranium and boron, which yield CO_2 substantially in spite of the fact, that their oxides should be more stable than their chlorides. On the other hand it is obvious from free energy data, that the great stability of the oxides of aluminium, chromium and silicon as compared to that of their chlorides, prohibits their participation in our reaction. It may be seen, that by comparing values of free energies, we may predict whether a certain cationic element will yield CO_2 by our method.

Procedure

A sample containing 0·2–0·3 mmoles of O_2 (e.g. 10 mg of CuO or 4 mg of H_2O) are introduced into a 2 ml Pyrex glass ampoule with a break-off tip and a seal-off constriction together with 100–200 mg of analytical, vacuum dried, 1 : 1 mixture of $HgCl_2$ and $Hg(CN)_2$. Utmost care should be taken to avoid any moisture getting into the ampoule or into any of the materials involved; dry oxides or salt should preferably be loaded in a dry-box, and small water samples should be introduced on the vacuum line by condensation. These precautions may be avoided if larger samples are taken, but it is not necessary to increase the amount of the $HgCl_2$–$Hg(CN)_2$ mixture as long as larger amounts of CO_2 are not required.

After introducing the sample and the reagent mixture, the ampoule is evacuated to about 10^{-3} mm Hg and is sealed off. Next it is heated to 400°C for 2 hr in a thermostated furnace. After cooling off, the ampoule is opened on the vacuum line and the gases formed are condensed by liquid nitrogen into a second ampoule of the same type containing 1·5–2 g of saturated zinc amalgam. The non-condensible

* Our procedure has been lately modified by Prof. RITTENBERG, who uses paracyanogen instead of mercuric cyanide.

gases formed—nitrogen and carbon monoxide—are pumped off. It should be noted, that the formation of carbon monoxide, the yield of which increases with temperature, is a loss of oxygen for analysis. The average yield of CO_2 obtained under the given conditions is some 20 per cent of the theoretical, calculated for the oxygen of the sample; the yield increased to 50 per cent when samples of 0·1 mmole or less were analysed.

The second ampoule containing the condensible products of the reaction over saturated zinc amalgam is sealed off under vacuum and is heated for 2 hr at 200°C. By this time all the $(CN)_2$ and HCl have been converted to $Zn(CN)_2$, $ZnCl_2$ and H_2 respectively. The ampoule is now ready for mass spectrometric analyses. If the sample originally contained hydrogen, there will be some hydrogen gas in the second ampoule, this may be pumped off on the mass spectrometer line after condensing the CO_2. Using this procedure, the impurity gases introduced into the mass spectrometer with the CO_2 are less than 0·1 per cent, determined mass spectrometrically.

Results

Table 1 presents a selected summary of our analytical results. The results obtained by our method are compared with the isotopic composition of the labelled compound obtained by thermal decomposition of the sample, or from analysis of the water from which the labelled compound was prepared. All water analyses which are used here for comparison, were done by the hypobromite–cobalt oxide method.[5] The results show correspondence between the two different determinations better than ±3 per cent. We should bear in mind that we measured CO_2 in one case, and O_2 in the other, each method having its own factors of error. Still it should be noted, that

TABLE 1. Analysis of oxides and salts

Compound	% O^{18} by the $HgCl_2$–$Hg(CN)_2$ method	% O^{18} by another method	% Difference	Method
HgO	9·15	9·23	−0·9	Thermal decomposition
HgO	76·6	75·8	+1·1	Thermal decomposition
MnO_2	8·9	8·82	+0·9	Thermal decomposition
PbO_2	1·45	1·40	+3·5	Thermal decomposition
PbO_2	7·56	7·67	−1·4	Thermal decomposition
CuO	7·17	7·31	−2·0	H_2O of preparation
CuO	2·40	2·35	+2·0	H_2O of preparation
CuO	2·35	2·35	0·0	H_2O of preparation
CuO	2·31	2·35	−1·7	H_2O of preparation
CoO	6·87	7·31	−6·0	H_2O of preparation
CoO	2·78	2·72	+2·2	H_2O of preparation
CoO	2·67	2·72	−1·8	H_2O of preparation
CoO	2·69	2·72	−1·0	H_2O of preparation
Fe_2O_3	6·46	6·50	−0·6	H_2O of preparation
Fe_2O_3	6·51	6·50	+0·1	H_2O of preparation
Fe_2O_3	11·60	11·65	−0·5	H_2O of preparation
Fe_2O_3	11·58	11·65	−0·6	H_2O of preparation
$BaSO_4$	1·97	2·07	−5·0	H_2O of preparation
$BaSO_4$	2·11	2·07	+2·0	H_2O of preparation
$BaSO_4$	2·09	2·07	+1·0	H_2O of preparation
$Ba(PO_4)_2$	2·17	2·06	+5·0	H_2O of preparation
$Ba_3(PO_4)_2$	1·87	2·06	−10·0	H_2O of preparation
$Ba_3(PO)_2$	1·93	2·06	−6·0	H_2O of preparation
$Ba_3(PO_4)_2$	2·01	2·06	−2·5	H_2O of preparation
$Ba_3(AsO_4)_2$	1·95	1·98	−1·5	H_2O of preparation
$Ba_3(AsO_4)_2$	2·02	1·98	+2·0	H_2O of preparation
$Ba_3(AsO_4)_2$	1·93	1·98	−2·5	H_2O of preparation
$(UO_2)_2Fe(CN)_6$	5·39	5·51	−2·4	H_2O of preparation
$(UO_2)_2Fe(CN)_6$	5·40	5·51	−2·4	H_2O of preparation
$(UO_2)_2Fe(CN)_6$	5·44	5·51	−1·4	H_2O of preparation

TABLE 2. Analysis of water by the $HgCl_2$–$Hg(CN)_2$ method

Amount of H_2O (mg)	% O^{18} by $HgCl_2$ method	O^{18} by HOBr–Co method	% O^{18} by CO_2 equil.
200	2·24	2·28	
200	2·19	2·28	
200	2·22	2·24	
3	2·21	2·24	
3	2·19		
3	2·22		
4	4·12	4·08	3·97
4	4·21	4·06	4·25
4	3·98	4·06	
200	9·39	9·27	9·40
200	9·29	9·27	
200	9·37	9·35	
3	9·21	9·30	9·43
3	9·17		
3	9·30		
200	22·1	22·4	21·9
200	22·3		
4	21·05		
4	21·15		
200	41·7	42·2	
200	41·9		

some compounds like $Ba_3(PO_4)_2$ give less reproducible results than others, which may be due to non-homogeneity of our labelled material or to its not being completely dry. The samples of iron oxide and uranyl ferrocyanide that have been prepared more carefully for some other applications, show much better correspondence, thus we do suggest, that the reproducibility of our method must be better than ± 1 per cent.

The results of analysis of water samples by the $HgCl_2$–$Hg(CN)_2$ method are summarized in Table 2. We do see here the same degree of correspondence as in Table 1. It should be noted, that there is better agreement in both Tables between samples containing a high percentage of O^{18}, which points to factors of error in the mass spectrometric determination; it excludes factors of isotopic dilution. Next it should be noted, that changing the amount of water in a sample by a factor of fifty or more, has practically little effect on the results of the analysis, though we do observe that in all cases the 3–4 mg samples show lower results by some 1–2 per cent, which in this case may be attributed to isotopic dilution.

Appendix—Methods of preparation of O^{18}-labelled compounds

CuO, Co_2O_3, Fe_2O_3 were prepared by drying and heating the corresponding hydroxides which were precipitated in H_2O^{18}.

AgO and HgO were also precipitated from H_2O^{18}.

PbO_2 was prepared electrolytically in H_2O^{18}.

MnO_2 was precipitated from a manganous solution with hypobromite.

$H_2SO_4{}^{18}$ has been prepared by oxidizing elementary sulphur in H_2O^{18} with elementary bromine. Later $BaSO_4$ was precipitated.

$H_3PO_4{}^{18}$ was prepared by hydrolysing PCl_3 in H_2O^{18} and oxidizing the product with bromine. Later the solution was neutralized by addition of metallic sodium and then $Ba_3(PO_4)_2$ was precipitated. $Ba_3(AsO_4)_2$ was prepared analogously to $Ba_3(PO_4)_3$ using $AsCl_3$.

$(UO_2)_2Fe(CN)_6$ was prepared by precipitating this salt from an $UO_2(NO_3)_2$ solution in H_2O^{18} which has been left to equilibrate for 24 hr. The salt was dried under vacuum; no $Hg(CN)_2$ was added to these samples. It is worth mentioning here, that we have tried to precipitate uranyl ions in the form of ammonium uranate, later igniting it in an oxygen-free atmosphere to U_3O_8. We get in this case quite irreproducible results which were always much lower than expected. We believe that some basic nitrate is co-precipitated and during the ignition to U_3O_8 there occurs oxygen exchange between the uranyl and nitrate ions.

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Gamma-ray Locating Device

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A problem which often arises in the building industry is that of projecting with precision a fixed mark on one side of a thick concrete slab through to the other side when it is difficult to use the theodolite or reference-grid method. The possibility of using a

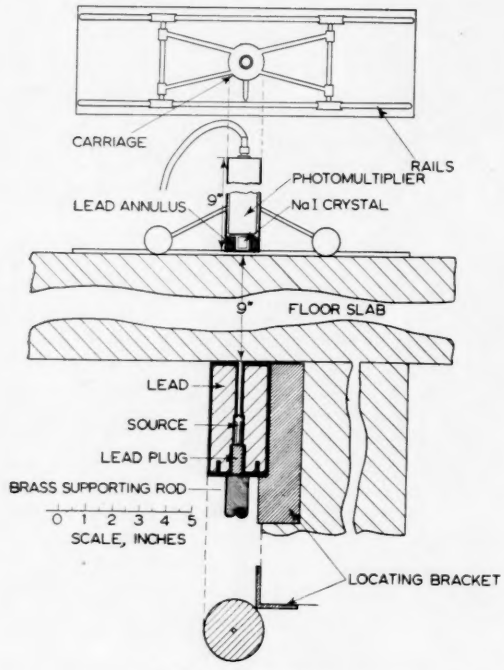

FIG. 1. Apparatus.

collimated beam of gamma radiation and a suitable detector has been investigated as an alternative method.

Method

The problem which initiated the investigation was the accurate alignment of concrete columns on successive floors of a building. It is vital that the base of a column on any floor should be vertically above the top of the column on the floor below. A feature of some modern buildings is that the concrete floor and part wall must be cast at the same time. Under such conditions the walls are erected before the columns on each floor thus sightings through the building from an open end are impossible, and the reference-grid method difficult to apply. Tell tales or fine holes through the reinforced concrete floor although providing positive location may not be permitted or could considerably weaken the structure.

A finely collimated beam of penetrating gamma radiation from a radioactive source located in turn at the corners of the top of the column below, when detected on the floor above, provides a means of "projecting" the outline of the column through the floor. A sketch of the apparatus is shown in Fig. 1. A scintillation counter was used as the detector. It consisted of a crystal of NaI (0·35 in. in diameter and 0·5 in. long) shielded in a lead annulus (0·50 in. long, 1·0 in. outside diameter) a photomultiplier* and a portable battery operated ratemeter.† Alignment simply involved placing the collimator at the corner of the lower column, close to the soffit (ceiling) and making a search on the floor above with the scintillation counter mounted in a vertical position with the crystal almost in contact with the floor, until the peak was found. The source employed was Cs^{137}.

Choice of source and detector

The factors to be considered in the choice of gamma-ray energy are first the attenuation of the radiation in concrete and secondly the thickness of lead shielding required to collimate the source and reduce the dose rate to the tolerable level. With these criteria Cs^{137} and Co^{60} were compared as possible gamma-ray sources. The narrow beam absorption coefficients in concrete for Cs^{137} and Co^{60} are 0·076 and 0·055 cm^2/g respectively; in lead the corresponding coefficients are 0·115 and 0·059 cm^2/g. Using these figures it can be calculated that the attenuation of Cs^{137} gamma rays in traversing 9 in. of concrete is only 3 times greater than that of Co^{60} gamma rays. In 2 in. of lead the attenuation is 15 times higher for Cs^{137} than for Co^{60}. The source chosen was therefore Cs^{137}, because a source to provide a given gamma-ray counting rate through the concrete floor was more easily screened and collimated when using this isotope. It was found

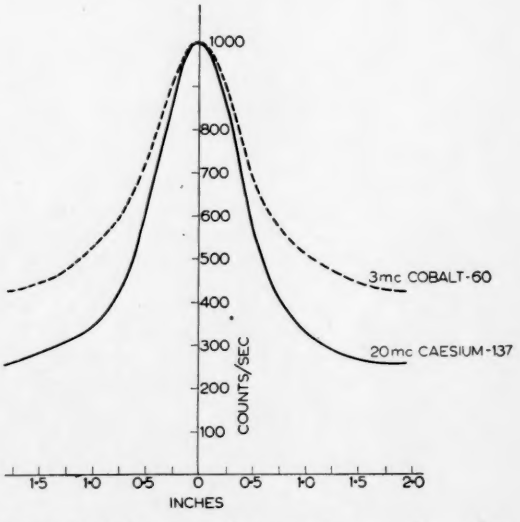

FIG. 2. Variation in counting rate across γ-ray beam after penetrating 9 in. of concrete.

* E.M.I. Electronics Ltd., Type 9524 B.
† Harwell Type 1320.

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that 50 mc produced a counting rate of 900 per second through 9 in. of concrete with the apparatus described above. A scintillation counter was chosen because even a small volume crystal has a high efficiency for detecting gamma radiation and therefore the peak counting rate can be accurately located.

Experimental results

Fig. 2 shows the counting rates obtained in scanning across a gamma-ray beam after penetrating through 9 in. of concrete and illustrates the superior collimation of Cs^{137} as compared with Co^{60}.

In operation, the approximate position of the emergent beam was easily found. To locate it accurately, the detector was mounted on a carriage and moved along rails placed near the beam. From the position of maximum counting rate a line was drawn on the concrete floor perpendicular to the rails; this should pass through the centre of the beam. By moving the rails to make a series of traverses in different directions, a series of perpendiculars were drawn. Ideally these should be concurrent at the beam centre. Typical measurements indicate that they are in fact nearly so and that the beam centre is located within about 1/16 in.

A field test with the instrument showed that the method suffered no serious loss in accuracy even though as many as three intersecting 1 in. diameter steel reinforcing bars were present in the concrete, and the results agreed with theodolite measurements.

Acknowledgements—This work was instigated by Mr. WOOLACOTT of Percy Bilton Ltd., and the authors gratefully acknowledge the encouragement and assistance which he gave in the course of the investigation.

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book reviews

The Nuclear Handbook: Consulting Editor O. R. Frisch: Newnes, London, 1958. xv + 640 octavo pp. 50s.

Nuclear scientists of ten or twelve years ago still carried the basic data of their own and related fields in loose-leaf notebooks in their pockets. As the subject grew, more and more branches of it were correlated and published in the form of reference books, till an adequate coverage of the whole field of pure and applied nuclear science could be accommodated only in a large library. At the same time the work of the individual scientist has become more specialized and only in popular volumes is an overall coverage of nuclear applications attempted.

The present book aims to fulfil a long felt need for a compilation of technical and scientific knowledge, covering a wide field of nuclear research and application and undertakes the formidable task of compressing the information within a handbook of manageable size. Such a compilation can be made either as a monograph or as a collection of annotated tables. This book uses both approaches, the tables giving the detailed information required by the specialist, the brief articles introducing the essentials of the various subjects.

Nineteen sections, covering most of the physical aspects of nuclear power and radioisotopes are contributed by 22 specialist authors, some of whom are acknowledged authorities in their own fields. Separate sections are devoted to: *Elements and isotopes* (section 3), *Natural radioactivity* (4), *Charged particles* (8), *X-rays and gamma rays* (9), *Fission product and transuranic elements* (11), *Ionization chambers and counters* (14), *Electronics* (15), *Nuclear emulsions* (18), *Cloud and bubble chambers* (17), and *Radiation effects and protection* (2). The comprehensive table of isotopes in section 3, complete with preferred breakdown schemes and compiled from up-to-date publications, is particularly valuable for reference. It is a pity that although particle percentages are given, relative gamma ray intensities are omitted through lack of space. The repetition of breakdown schemes on different pages, however convenient, might have been sacrificed to make room for these. The tables of *Thermal neutron cross-sections* (section 10) and of *Fission product yields* (section 11) are also very valuable in assessing the practicability of using particular isotopes.

The inclusion of industrial sources of supply of instruments and materials emphasizes that this is a book for practical use, as also do Sections 8 on *Vacuum* and 16 II on *Solenoids, magnets and magnetic fields*. However the purist should find satisfying theoretical erudition in the 67 pages of section 19 on *Nuclear reactions*.

An account of the U. K. Atomic Energy Authority at the beginning of the book may give an impression that it is insular, an impression which is strengthened by the fact that British sources of supplies and British health regulations are quoted. This would be unfortunate, since the bulk of the handbook deserves wider circulation.

The balance of subject matter in such a comprehensive survey must be a matter for personal editorial decision, but it is gratifying to find such a large proportion of the work dedicated to subjects of direct consequence to isotope users. Most of the authors have felt the lack of space acutely; in general this has stimulated them to achieve wonders of conciseness, though sometimes oversimplification has resulted and occasionally plain misstatement. Section 13 on *Chemistry* is limited to 15 pages and although the author has compressed a great deal of information into the available space, his account of *Chemical and other effects of radiation* suffers by not distinguishing conjectural and actual applications, by lumping together such unrelated techniques as control of screw-worm fly and wood-boring insects, and by identifying trichinosis with tape worm. Section 14 is similarly inadequate when dealing with Geiger counters; Fig. 1 is misleading through the omission of a logarithmic scale, and statements about pulse amplitude in the G. M. region and about the nature of dead-time are inaccurate. Following this, Section 15 on *Electronics* is a model of concise and lucid presentation, though it does take 43 pages.

The level of presentation is reasonably uniform, but the references are not. No general policy seems to have been adopted as to the quoting of general bibliographies or definitive articles. References in the various sections vary in number from 91 to none at all and all possible methods of quoting seem to have been used indiscriminately.

The index in 11½ pages is only adequate if taken in conjunction with the detailed table of contents (e.g. a reader wishing to refer to "Thermal neutron cross-sections" must find them under "Thermal", not under "Neutron"). Doubtless readers will soon know their way about the handbook.

The book is well produced with few misprints and a strong binding which will have to withstand hard wear. The general impression is that it contains a wealth of information, well presented, in surprisingly small space. The octavo pages make it a handy little volume which should find a valued place in all nuclear laboratories.

J. L. Putman

HEINRICH FASSBENDER: **Einfuhrung in die Messtechnik der Kernstrahlung und die Anwendung der Radioisotope.** Georg Thieme Verlag, Stuttgart, 1958. 223 S. DM 37.50.

DER behandelte Stoff ist in 4 Abschnitte gegliedert, die bei dem gewählten Umfang des Buches naturgemäss mit recht verschiedener Ausführlichkeit behandelt wurden. Die Einleitung macht den Laien mit einigen Grundbegriffen der Kernphysik,-chemie u. -technik bekannt. In den beiden folgenden Hauptabschnitten werden Strahlungsmessgeräte bzw. ihre Anwendung bei der Verwendung der verschiedenen Radioisotope besprochen. Nach einem kurzen Hinweis auf die historische Entwicklung werden die physikalischen Grundlagen, Fehlerberechnung und ähnliche messtechnische Einzelheiten bzw. Anwendungsbeispiele gegeben. In ähnlicher Weise wird der letzte Abschnitt über Strahlenschutz behandelt. Einige harmlose Druckfehler z.B. auf den Seiten 111. 123, 175 könnten auch bei dem Laien, der das Buch benutzt kaum Verwirrung hervorrufen. Bedenklich könnte ohne Angabe näherer Einzelheiten aber die Berechnung der Ausgangs-Aktivitäten an C^{11} in dem Versuch über die Verdaulichkeit von Butter und Margarine stimmen. Der Fachmann erhält einen ziemlich bunten Überblick über die Leistungsfähigkeit der Firma Friesecke & Höpfner sowie einiger anderer Firmen.

F. STRASSMANN

P. J. DJATSCHENKO u.a.: **Verschleissuntersuchungen mit Hilfe radioaktiver Isotope.** V. E. B. Verlag Technik Berlin 1959. Deutsche Redaktion Dipl. Ing. Gerd Fleischer, Dresden. (Preisangabe fehlt).

AN Hand von 15 Aufsätzen über die Verschleissprüfungen von Gleitpaarungen, Schneidewerkzeugen etc. erhält der Betriebsingenieur einen recht interessanten Einblick in die Arbeits- und Messmethodik, die für das Arbeiten mit radioaktiven Isotopen vorgesehen ist. Im einleitenden Aufsatz wird zwar auf die verständlicher Weise noch vorhandenen Unvollkommenheiten der Methoden hingewiesen, doch setzen die in den weiteren Aufsätzen vorgeschlagenen Methoden eine gründliche praktische und theoretische Beherrschung der radioaktiven Arbeitsmethoden voraus, ohne dass dieser wichtige Umstand betont wird. Das gleiche gilt auch für alle Fragen des Strahlenschutzes für den der Betriebsingenieur verantwortlich ist. Treffen diese Voraussetzungen nicht zu, so dürften die experimentellen Ergebnisse vielfach von äusserst zweifelhaftem Wert sein und die mögliche Gefährdung der Arbeite rzu ernsten Bedenken Anlass geben.

Das Buch ist mit zahlreichen, interessanten Diagrammen, Tabellen, Skizzen und Photographien ausgestattet. Bei einer Neuauflage wäre die Wahl einer grösseren Type im Interesse eines klareren Textbildes dringend zu empfehlen.

F. STRASSMANN

Radiation Biology and Medicine. Edited by WALTER D. CLAUS. Addison–Wesley Publishing Company, Reading, Massachusetts, U.S.A., 1958. xx + 944 pp. 92s.

THIS book was prepared for the United States Atomic Energy Commission (which holds the copyright) and was presented at the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958. It contains a series of reviews by American authors of advances in U.S. thought and research in selected topics on the effects and uses of radiation in the life sciences. The main text consists of ten parts, each of one or more chapters. Part 1 is a general introduction, and the remaining nine have the following titles: basic mechanisms of biological reaction to radiation; mutational effects of radiation; mathematical biology; mammalian response to radiation; radiation safety; medical uses of atomic radiation; agricultural uses of radiation; tracer applications; instrumentation and dosimetry. In addition there are two appendices: appendix A lists the libraries throughout the world in which reports of the United States Atomic Energy Commission can be found, and appendix B is a list of recent and current unclassified research contracts and grants in radiation effects and usage supported by the United States government and various private agencies in the United States.

Many readers will treat this book a as supplement to A. HOLLAENDER's *Radiation Biology*; indeed, many of the names of contributors are common to both. Being a single volume, albeit of nearly a thousand pages, it is much shorter than *Radiation Biology*, and the chapters are more compressed. Furthermore, the two do not cover exactly the same ground. A big virtue of the new volume is that (thanks, no doubt, to the enormous resources of the U.S.A.E.C.) it has escaped the usual fate of volumes consisting of reviews by numerous contributors: publication has followed very shortly after the reviews were written. The bibliographies all contain references to literature published in 1958.

When a volume consists of reviews by more than

fifty contributors, it is almost inevitable that there should be some variation in standard of writing and breadth of outlook. This book is no exception. CURT STERN's chapter on radiation and population genetics is a model that might well be emulated by others faced with the difficult task of reviewing a large and difficult subject in a small space; and the chapter by WALTER D. CLAUS on the concept and philosophy of permissible dose to radiation is a clear exposition of the American approach to this subject. A less favourable impression is received from the chapter on the mathematical approach to fundamental phenomena in biology, by N. RASHEVSKY of the Committee on Mathematical Biology, University of Chicago. His definition of mathematical biology is very narrow: it excludes, for example, the work of R. A. FISHER and his school. This reviewer believes that most biologists would consider FISHER's book *The Genetical Theory of Natural Selection* to be an example of mathematical biology *par excellence*. Clearly the reader will have to exercise judgment when making use of this book, and he should bear in mind that its primary intention is to review American thought and research; but this will not prevent it from being a useful volume to anyone in the field of radiation research.

T. C. CARTER

WILLIAM H. SULLIVAN: **Trilinear Chart of Nuclides.** U.S. Government Printing Office, Washington 25, D.C., 1957, 4 pp + chart. $2.00. (reviewed in *Int. J. Appl. Rad. Isotopes* **4,** 127 (1958).)

THE U.S. Atomic Energy Commission announces a new service to owners of the *Trilinear Chart of Nuclides*. Revision sheets are now issued for keeping the basic chart up to date.

Each Revision Sheet issue consists of revised hexagons for a maximum of 49 nuclides, printed on an $8\frac{1}{2} \times 11$-in. gummed sheet. The arrangement of individual hexagon "stamps" on the sheet minimizes the amount of cutting required to free them for affixing—as one would postage stamps—to the *Chart* at the proper nuclide positions.

The first issue, July 1958, covers significant data changes for the period July 1956 (the "cut-off" date for publication of the *Chart*) through June 1958. Subsequent sheets will be issued from time to time as warranted by the accumulation of new data—probably on the order of two to four times per year.

This service is being offered initially on an indefinite subscription basis for $1.00, and renewals will be solicited at such time as it is determined that the income received from subscriptions has been expended on costs of the Revision Sheet service.

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international news

OEEC

Symposium on Technical Methods of Health Protection in Atomic Energy Installations
May 1959, *at Risø (Denmark)*

A SYMPOSIUM intended for health physicists of atomic energy centres or installations is being organized by the OEEC European Nuclear Energy Agency and the Danish Atomic Energy Commission, in co-operation with a number of experts from Europe, from the United States and from Canada.

The purpose of the symposium is to discuss scientific and technical aspects of health physics in atomic installations (radiation protection, control of radioactive contamination, emergency measures).

The symposium will be held from 25 to 28 May at the Danish Atomic Energy Commission research centre at Risø, near Copenhagen.

Further information may be obtained from:

OEEC
European Nuclear Energy Agency
38 Boulevard Suchet
Paris 16.

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forthcoming papers

G. Courtois et J. Lecomte: Marquage d'abeilles au moyen d'or radioactif.

A. M. Baptista, A. J. G. Ramalho and A. M. de Matos Fernandes: Photoradiochromatography. Method for the study of chromatograms with radioactive substances.

W. S. Broecker, C. S. Tucek and E. A. Olson: Radiocarbon analysis of oceanic CO_2.

Robert L. Bell and George J. Hertsch: Automatic contour scanner for myelography.

Milton G. Crane, John E. Holloway, Ralph Adams and Ivor C. Woodward: The relative flow rates of red cells and plasma. Peripheral and central circulation studies in the dog.

J. S. Robertson, V. P. Bond and E. P. Cronkite: Resolution and image spread in autoradiographs of tritium-labeled cells.

R. A. Oppermann, R. F. Nystrom, W. O. Nelson and R. E. Brown: Use of tertiary alkyl primary C_{12}–C_{14} amines for the assay of $C^{14}O_2$ by liquid scintillation counting.

F. J. Domingues, K. J. Gildner, R. R. Baldwin and J. R. Lowry: An instrument and technique for the continuous measurement of respiratory CO_2 patterns in metabolic tracer studies.

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International Journal of Applied Radiation and Isotopes. 1959, Vol. 5, pp. 243-252. Pergamon Press Ltd. Printed in Northern Ireland

Investigations of Radio-yttrium (Y^{90}) Metabolism

Studies of Organ-distribution with Special Regard to the Radioautographic Method of Demonstration and to Paper Electrophoresis under Various Experimental Conditions

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(*Received* 14 *November* 1958)

By means of the usual measurement methods the organ distribution of Y^{90} ($Y^{90}Cl_3$) was examined under various experimental conditions. Special emphasis was put on the inclusion of all organs. A further elucidation of Y^{90} metabolism in regard to the question of structurally differentiated distribution following different methods of administration was achieved by using the radioautographic method of demonstration and also by using electrophoresis with subsequent registration of activity curves.

In surveying the whole complex of our examination results, we see that Y^{90} can by no means be called a "bone seeker" during the first 8 days, a period which is of great radiobiological importance. Within this period we never find more than 30 per cent of the dose in the skeletal system. On the other hand, there are high specific activities, depending on the method of administration, in the metabolically important organs, such as the pancreas, the hypophyses, and also in the genitals. The radioautographical pictures show that the variations in distribution are the result of the different transport mechanisms. Thus we assume that after intraperitoneal injection transport takes place mainly by way of the lymph. Furthermore, radioautography makes clear the formation of complexes on the part of yttrium and the nucleic acids; the relation between yttrium and the phospholipoids is also confirmed by a closer examination of the individual lipid fractions.

From the point of view of radioactive contamination, the accumulation of Y^{90} in the genitals, especially the ovaries, is important. The excretion of the radioisotope which we found in the lung seems to us important in so far as the lung is shown to function as an organ of the reticuloendothelial system; furthermore, the possibility of recontamination in animal experiments must be kept in mind.

Thus our distribution studies of Y^{90} produced results which are not only important in the question of incorporation–decorporation, but which also point to further medical and biochemical problems.

DES RECHERCHES SUR LE MÉTABOLISME DU RADIO-YTTRIUM (Y^{90}). ÉTUDES DE LA DISTRIBUTION DANS LES ORGANES, AYANT REGARD PARTICULIER À LA MÉTHODE DE DÉMONSTRATION RADIO-AUTOGRAPHIQUE ET À L'ÉLECTROPHORÉSIE SUR PAPIER SOUS DES CONDITIONS EXPÉRIMENTALES VARIÉES

La distribution d'Y^{90} ($Y^{90}Cl_3$) dans les organes fut étudiée sous des conditions variées par les méthodes de mesure habituelles. On s'efforça d'inclure tous les organes. On acheva une élucidation ultérieure du métabolisme d'Y^{90}, en rapport à la question de la différentiation structurelle de la distribution suivant les différentes méthodes d'administration, en utilisant

la méthode de démonstration radio-autographique, ainsi que l'électrophorésie avec enregistrement des courbes d'activité.

La revue de la complexité totale des résultats de nos examens montrent que dans les huit premiers jours l'Y^{90} est loin d'être un "chercheur d'os", et cette période a une grande importance radio-biologique. Dans cette période on ne trouve jamais plus de 30 pour cent de la dose dans le système squelettique. Par contre, il y a de fortes activités spécifiques, variant selon la méthode d'administration, dans les organes d'importance métabolique, tels que les pancréas, les hypophysies ainsi que les organes génitaux. Les images radio-autographiques montrent que les variations de distribution prennent suite des différents mécanismes transportatifs. Ainsi on suppose que, suivant une injection intrapéritonéale, la transportation se fait principalement par la lymphe. De plus, la radio-autographie rend évidente la formation de matières complexes de la part de l'yttrium et des acides nucléiques; le rapport entre l'yttrium et les phospholipidiques est aussi vérifié par une inspection plus précise des fractions lipides particulières.

Du point de vue de la contamination radioactive, les rassemblement de l'Y^{90} dans les organes génitaux, surtout dans les ovaires, est d'importance. L'excrétion du radioisotope trouvé dans le poumon nous paraît important d'autant que le poumon se voit fonctionner comme un organe du système réticuloendothélial; en outre, il faut tenir en vue la possibilité de la récontamination dans les expériences avec des animaux.

Ainsi nos études sur la distribution de l'Y^{90} ont donné des résultats non seulement importants à la question de l'incorporation-décorporation mais aussi indicatifs de problèmes ultérieurs de la médecine et de la biochimie.

ИССЛЕДОВАНИЕ ОБМЕНА РАДИОАКТИВНОГО ИТТРИЯ ($У^{90}$). ИЗУЧЕНИЕ РАСПРЕДЕЛЕНИЯ $У^{90}$ ПО ОРГАНАМ ПРИ РАЗЛИЧНЫХ ЭКСПЕРИМЕНТАЛЬНЫХ УСЛОВИЯХ, С ИСПОЛЬЗОВАНИЕМ РАЗЛИЧНЫХ МЕТОДОВ, ОСОБЕННО РАДИОАВТОГРАФИИ И ЭЛЕКТРОФОРЕЗА НА БУМАГЕ

Распределение иттрия-90 ($У^{90}Cl_3$) по органам при различных экспериментальных условиях было изучено обычными методами; показано, что для иттрия характерно включение во все органы. Более углубленное исследование избирательного поглощения иттрия в различных структурах при разных способах его введения удалось далее осуществить с помощью метода радиоавтографии, а также электрофореза (с последующей регистрацией кривых электрофоретического распределения активности).

На основании всего комплекса полученных нами данных можно показать, что иттрий никак нельзя отнести к числу веществ, избирательно накапливающихся в костях в течение первых 8 суток, т.е. в течение периода, имеющего большое значение для проявления радиобиологического эффекта. В течение этого периода мы ни разу не обнаруживали в костях более 30% от введенной дозы. С другой стороны, в органах важных для обмена веществ—таких, как поджелудочная железа, гипофиз, а также гениталин—обнаруживаются высокие удельные активности, вариирующие в зависимости от метода введения. Радиоавтографическим методом показано, что вариации в распределении являются результатом различий в транспортных механизмах. Так, мы считаем, что после внутрибрюшинной инъекции транспорт осуществляется главным образом через лимфу.

Радиоавтографическим методом удается обнаружить также комплексообразование между иттрием и нуклеиновыми кислотами; связывание иттрия с фосфолипидами подтверждается при изолированном исследовании индивидуальных липидных фракций.

С точки зрения возможных радиоактивных загрязнений аккумуляция иттрия в гениталиях, особенно в яичниках, приобретает существенно важное значение. Не менее существенно обнаруженное нами выделение иттрия через легкие, поскольку легкие являются одним из органов ретикулоэндотелиальной системы; кроме того необходимо учитывать возможность вторичных загрязнений при работе с экспериментальными животными.

Таким образом наши исследования по распределению иттрия-90 дали результаты, существенные не только в отношении выяснения накопления и выведения иттрия, но и важные для дальнейших медицинских и биохимических проблем.

UNTERSUCHUNG DES RADIOYTTRIUM-STOFFWECHSELS. STUDIEN ÜBER ORGANVERTEILUNG MIT BESONDERER BERÜCKSICHTIGUGN AUTORADIOGRAPHISCHEN NACHWEISMETHODEN UND DER PAPIERELEKTROPHORESE BEI VERSCHIEDENEN EXPERIMENTELLEN BEDINGUNGEN

Mit Hilfe der üblichen Messmethoden wurde die Organverteilung von Y^{90} ($Y^{90}Cl_3$) bei verschiedenen Versuchsbedingungen untersucht. Eine weitere Beleuchtung des Y^{90}-Stoffwechsels im Hinblick auf Fragen der strukturell differenzierten Verteilung infolge verschiedener Verabreichungsmethoden wurde sowohl mit Hilfe von Autoradiographik als auch durch Verwendung von Elektrophorese mit nachfolgender Registrierung der Aktivitätskurven nachgewiesen.

Der Überblick über unsere gesamten Versuchsergebnisse zeight deutlich, dass Y^{90} während der ersten 8 Tage, das heisst wahrend eines Zeitraumes von grösster biologischer wichtigkeit, keineswegs als "bone seeker" bezeichnet werden kann. Andrerseits finden sich hohe spezifische Aktivitäten je nach Art der Verabreichung an den für den Stoffwechsel wichtigen Organen, wie z.B. Pankreas, Hypophyse und auch an den Genitalien. Die autoradiographischen Bilder zeigen, dass der Unterschied der Verteilung infolge verschiedener Transportmechanismen auftritt. So nehmen wir z.B. an, dass der Transport nach intraperitioneler Injektion hauptsächlich auf dem Lymphwege erfolgt. Des weiteren beweist die Autoradiographie dass Komplexbildung eines Teiles des Yttriums mit Nukleinsäuren stattfindet. Die Wechselwirkung zwischen Yttrium und den Phospholipoiden wird ebenfalls durch eine genauere Untersuchung der einzelnen Lipoidfraktionen bestätight.

Vom Standpunkt der radioaktiven Verseuchung ist die Ansammlung von Y^{90} an den Genitalien, besonders an den Ovarien, bedeutungsvoll. Die von uns aufgefundenen Ausscheidung dieses Radio-Isotops durch die Lunge erscheint insofern wichtig, als es zeigt, dass sie als Organ des Reticuloendothelial-Systems in Funktion tritt. Ausserdem muss mit der Möglichkeit einer Rückverseuchung der Versuchstiere gerechnet werden.

Die Ergebnisse unserer Untersuchung über die Verteilung von Y^{90} sind daher nicht nur in Bezug auf die Aufnahme und Ausscheidung wichtig, sondern beleuchten auch weiter verschiedene medizinische und biologische Probleme.

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Our incorporation studies with Sr^{90} and experiments on intracavitary therapy with colloidal Y^{90} showed the necessity of clarifying the question of the metabolism of the radioisotope yttrium-90 (Y^{90}). The literature hitherto available on the subject contains certain contradictions, mainly as the result of differences in experimental conditions; e.g. the amount of tracer substance used in the injection plays an important part in such distribution studies.[1–5] In tracer-free injections the method of administration is not important,[6] but the situation is completely different when a tracer is used, as our own experiments show. Similarly, the results of such studies depend upon the kind of animal used.

In our experiments Y^{90} was used in a constant tracer addition of 0·05 mg Y^{+++}/1 mc; guinea pigs were used as experimental animals.

In addition to the determination of specific radioactivity (imp./min/g) and total organ radioactivity by the usual methods of measurement, radioautographs (stripping film method described by Graul *et al.*[15]) were made of each organ and electrophoretic analyses of serum protein and organ protein were carried out.

RESULTS

1. Organ-distribution and accumulation

The distribution of Y^{90}, injected as $Y^{90}Cl_3$, was examined in relation to time. Of the various methods of administration, we used intraperitoneal and intracardiac injections as well as oral administration by means of a stomach tube.

It was found that there are no differences in distribution with doses between 75 μc and 10 mc.

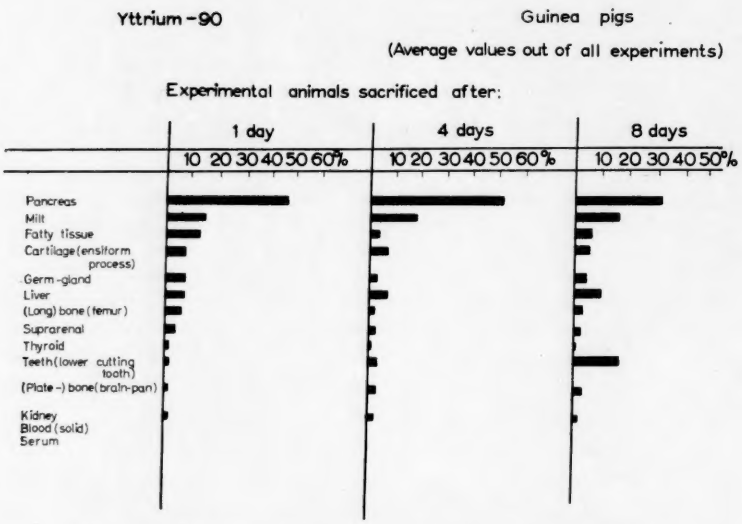

FIG. 1. Specific activity in individual organs following intraperitoneal injection (average value from 20 guinea pigs).

The various methods of administration produced the following modes of distribution:

1.1. Intraperitoneal injection. Since Y^{90} has a half-life of $\sim 2\frac{1}{2}$ days, the first 8 days after its administration are especially interesting from the radiobiological point of view. For this reason time intervals of 24 hr, 4 days, and 8 days were used for the individual examinations. We determined the specific and total radioactivity of the individual organs. Percentages were calculated by adding the specific and total activities respectively of all the organs examined and equating them with 100 per cent. The corresponding values of the individual organs were calculated percentually on this basis.

In regard to distribution following intraperitoneal injection, it can be stated without doubt that the greatest accumulation is found in the pancreas; the specific radioactivity here is in the range of 40 per cent (Fig. 1: average values from 20 intraperitoneal-injected animals). After 4 days a maximum value of 50 per cent is reached. High accumulation values were also found in other organs, especially parenchymatous organs. In regard to genetic damage, the accumulation of Y^{90} in the reproductive organs must be particularly noted; of the 20 organs examined, the genitals rank fifth. Here there is a striking difference of distribution between the ovaries and the testes. We found that the specific activity in the female glands after intraperitoneal injection was $2\frac{1}{2}$ times as great as that in the testes. It is assumed that a hormonal factor plays an essential part here, since in the course of pregnancy we were able to demonstrate a change in the pattern of distribution and accumulation, without any noteworthy accumulation being found in the embryo. The size of the organ is naturally an important factor in the percentual distribution of total organ radioactivity; thus the liver, for example, occupies a particularly conspicuous position in such evaluations. However, from the radiobiological standpoint of organ damage due to Y^{90}-β-radiation, the specific activity must be considered the more important.

With regard to the relatively short half-life of yttrium, our experiments showed that bone cannot be considered a critical organ for Y^{90}. We found an accumulation of 25–28 per cent during the first 8 days. Here again, the reaction of female animals differs from that of males; the accumulation in females is 3·6 times greater than in males.

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Yttrium-91 with its longer half-life, naturally produces different results.[7,8,9]

1.2. Intracardiac injections. It is also impossible to speak of Y^{90} as a "bone seeker" following intracardiac injection, since the average value of the accumulation in the skeletal system of all the intracardiac-injected animals was 27·1 per cent in the first 8 days. The pertinent values for specific activities here are quite different from those following intraperitoneal injection. Whereas the pancreas diminishes in importance, we found a particularly high specific radioactivity in the hypophyses of these groups of animals. In general the endocrine glands show greater accumulation after intracardiac injection than after intraperitoneal injection (Table 1).

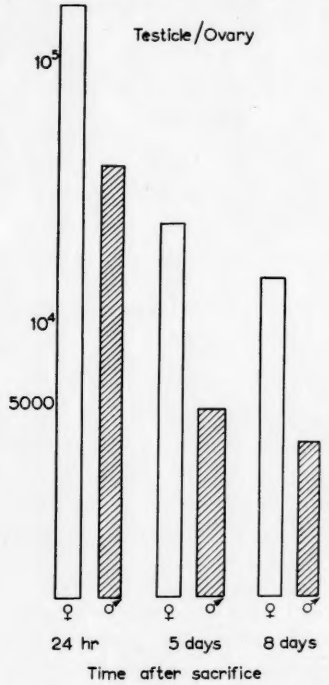

FIG. 2. Comparison of specific activity in male and female genitals (guinea pigs).

Since Y^{90} at physiological pH forms insoluble hydroxides which easily turn into colloids,[6,10–14] a special affinity with the reticuloendothelial system is to be expected. This is shown by the relatively high specific activity of the liver and the spleen (Table 2). The radioautographic findings also point in this direction. Thus in the liver particularly high values are found in the Kupffer's cells.

TABLE 1

Organ	1st day	4th day	8th day
Hypophyses	24·0%	28·1%	14·1%
Thyroid gland	2·1%	1·5%	1·5%
Pancreas	1·3%	0·5%	2·3%
Suprarenal gland	1·3%	0·8%	3·7%
Testes	0·2%	0·5%	0·2%
Total	28·8%	31·4%	21·8%

1.3. Oral administration. Yttrium-90 chloride was administered to animals by means of a stomach tube. Under these experimental conditions there was a resorption of 51 per cent, which was distributed in the animal organism as follows: in the skeletal system we found 0·7 per cent organ activity after 24 hr, 10·5 per cent after 4 days, and 15·3 per cent after 12 days.

The marked accumulation of Y^{90} in the gastrointestinal tract 24 hr after administration decreased noticeably after 4 days; after 12 days no activity worth mentioning could be demonstrated. Of the various sections of the intestine, the large intestine showed an especially high accumulation of 34·5 per cent in the first 24 hr. Furthermore, a high total radioactivity of ~45 per cent was found in the muscles of animals killed after 4 and 12 days.

A survey of the specific accumulation in the individual organs following oral administration reveals strikingly high values in the hypophyses. In the animals killed after 24 hr

TABLE 2

Organ	1st day	4th day	8th day
Bone	10·5%	9·5%	8·6%
Liver	8·0%	6·0%	8·0%
Spleen	7·8%	2·1%	20·0%
Kidney	9·8%	3·1%	3·0%
Lung	3·3%	0·7%	1·8%

the hypophyses showed the highest specific radioactivity (6·5 per cent; Table 3) of all organs except the stomach and intestine; the values for the liver and the spleen, for example, were 0·2 per cent. After 4 days the value for the hypophyses rose to 61 per cent. In contrast to the results obtained by intracardiac injection, oral administration did not produce any noteworthy activity in the other endocrine glands.

1.4. Intraperitoneal injection of charcoal-adsorbed Y^{90}. Yttrium-90 is particularly suited to intracavitary tumor therapy on account of its short half-life and its β-radiation. Here it is a question of the relative purity of Y^{90} in comparison with that of Sr^{90}, and also of the amount of Y^{90} which migrates to the organs. There are various possibilities of localizing the isotope; one of them is to adsorb it on charcoal particles of 40–60 μ diameter.

TABLE 3

Organ	1st day	4th day	8th day
Hypophyses	6·5%	65·0%	2·0%
Liver	0·2%	1·0%	18·0%
Spleen	0·2%	0·5%	12·2%

Our experiments showed that very little was transported away. Thus in the animal bodies, i.e. outside the abdominal cavity, we found 0·6 per cent of the dose after 24 hr, 0·9 per cent after 4 days, and 1·3 per cent after 8 days. The distribution pattern of these slight percentages is quite similar to that of $Y^{90}Cl_3$ after intraperitoneal injection, and therefore requires no further discussion.

2. Excretion

Important conclusions on yttrium metabolism can be drawn from its excretion in the feces and urine. By using metabolism cages in our experiments we found basically the same curve pattern in all the methods of administration in regard to the time and amount of excretion. Fig. 4 shows this type of curve. In all cases (50 animals) the excretion of yttrium in the feces was greater than that in the urine. But if excretion is considered from the point of view of total injected radioactivity, differences are found. Thus the excretory quota of animals which had received an intraperitoneal injection of 20 μc of $Y^{90}Cl_3$ was thirty times as high as that of animals which had received 10 mc. The amount excreted decreases tenfold after intraperitoneal injection of charcoal-adsorbed Y^{90}; i.e. after 8 days only 0·1 per cent is excreted in the feces and urine. Since the question of nutriment is important in such experiments, a standard food must be given.

Whereas yttrium excretion, in relation to the total radioactivity of the Y^{90} administered, is greater during the first 8 days after intracardiac injection (6·5 per cent) than after intraperitoneal injection (2·5 per cent), it is naturally greatest following stomach-tube administration (48·9 per cent).

3. Microradioautographic findings

In our distribution studies we found a certain difference in the accumulation of Y^{90} in the various organs, depending upon the method of administration. The question whether this difference is structural, or whether it is caused by the transport mechanism, was studied by means of radioautography. Here we used our own modification[15,16] of the stripping film method according to PELC,[17] which has the advantage of relative simplicity of handling, and also has a comparatively high resolving power. The findings discussed here are based on 760 radioautographic preparations.

Of the individual organs, the liver shows the special affinity of yttrium with the reticuloendothelial system (in this case Kupffer's cells), since yttrium is present as a colloid (Fig. 3). In this accumulation no quantitative differences could be found among the various methods of administration. Furthermore, Y^{90} can be demonstrated by radioautographs of the lumina of the blood vessels and bile ducts; here the time factor seems to make no difference. However, in regard to the accumulation of yttrium in the parenchymal cells of the liver, we found variations due to the time factor.

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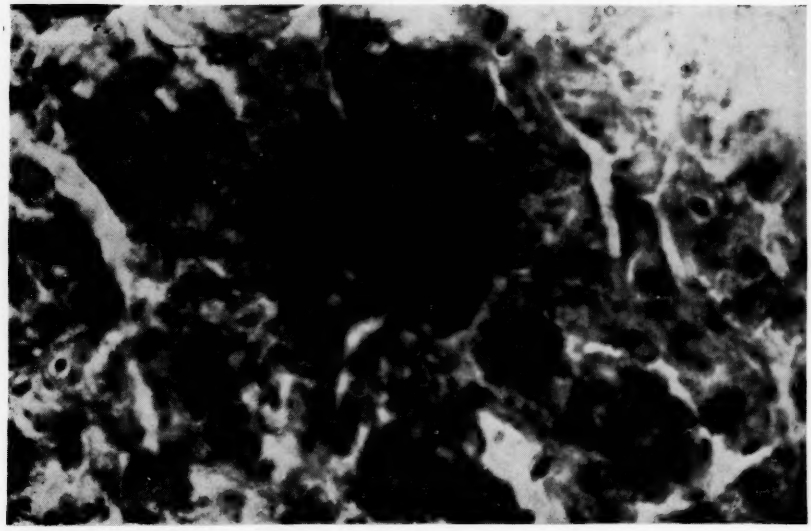

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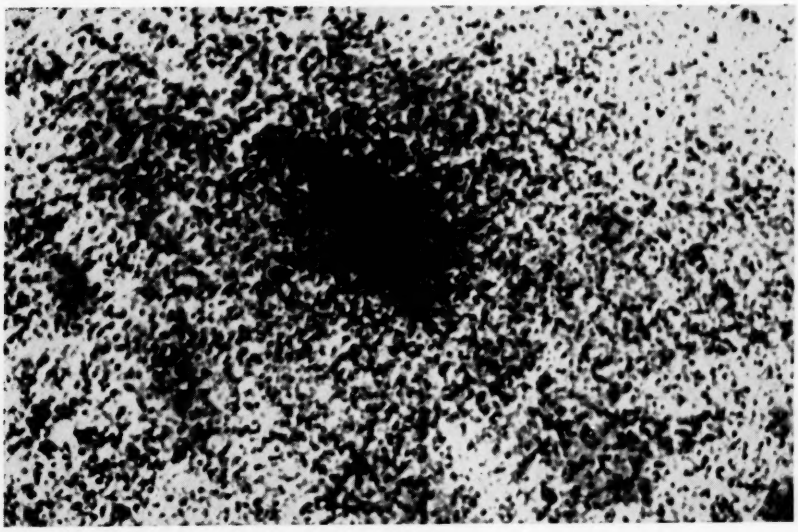
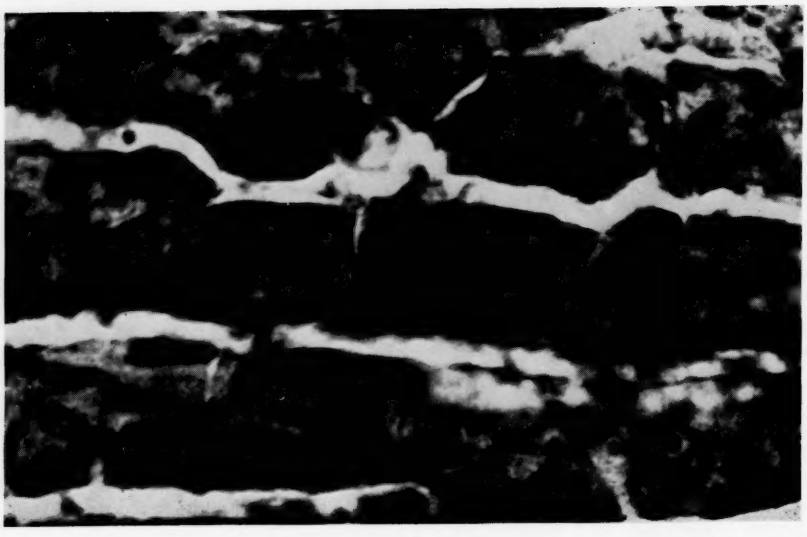


(b)

FIG. 3. Radioautography of a liver section of Kupffer's cells.
(a) Histology, (b) Radioautography ($\times$1200).



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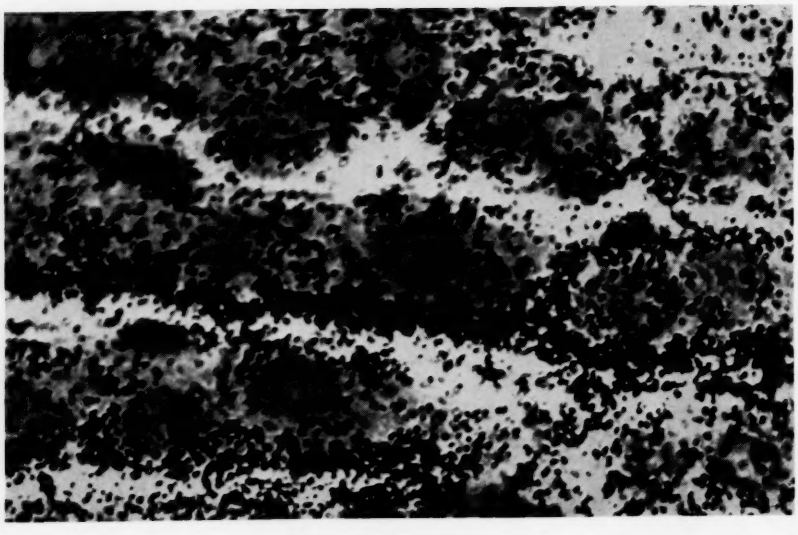

(b)

FIG. 5. Radioautography of liver cells. (a) Histology, (b) Radioautography (×1200).

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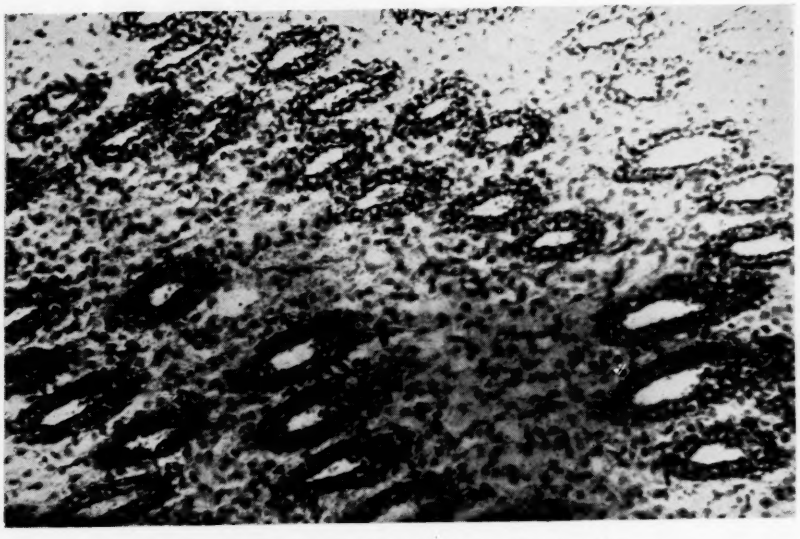


FIG. 6. Radioautography: Kidney, showing the zone of the straight collecting tubule (×400).

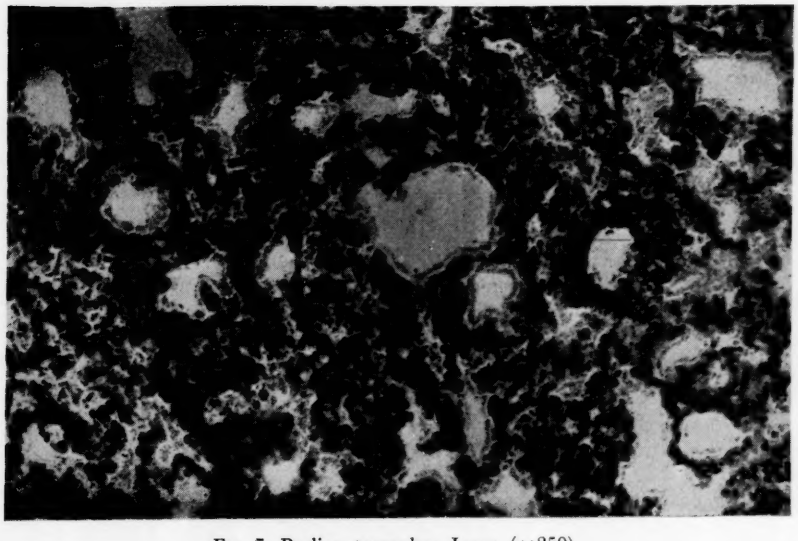
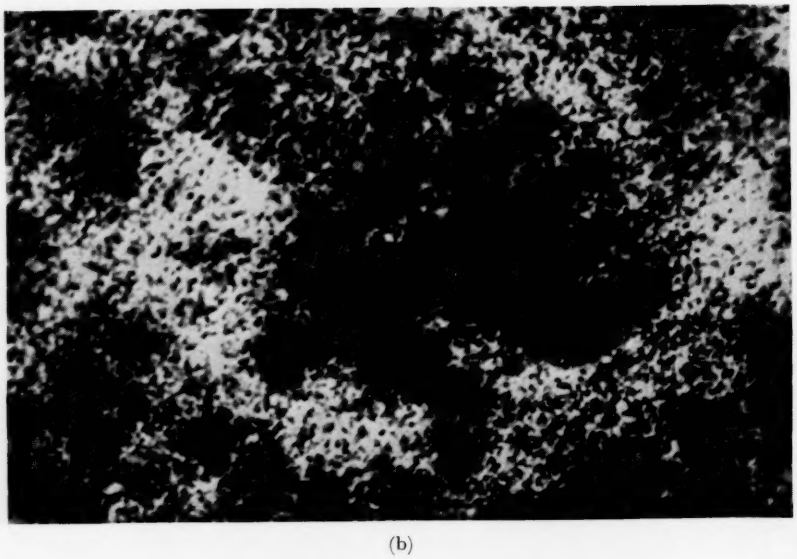


FIG. 7. Radioautography: Lung (×250).

(a)



(b)

FIG. 8. Radioautography: Hypophyses.
(a) Histology, (b) Radioautography ($\times 1200$).

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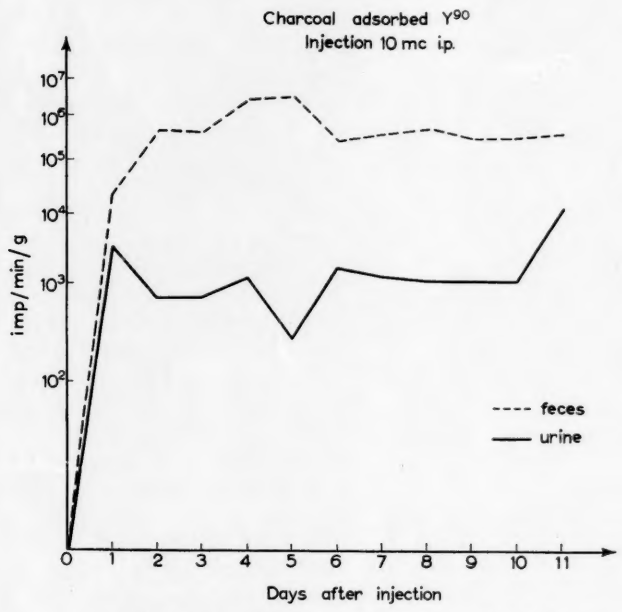


FIG. 4. Excretory curves; imp./min in relation to time.

After 24 hr there was still a diffuse distribution of radioactivity, but after 4 and 8 days respectively we found a noticeable accumulation of activity in the borders of the cells (Fig. 5). We were able to demonstrate an increased accumulation of lipoids and phospholipoids in these places; similar findings have also been made in the kidney and suprarenal gland.[18]

An increased diffuse radioautographic activity of the Malpighian corpuscles was found in the spleen preparations, independent of the time interval or method of administration.

In the kidney a strikingly strong concentration of yttrium in certain parts of the cells of the straight collecting tubules (Fig. 6) and the primary convoluted tubule is shown by radioautography; an accumulation of lipoids can also be found here.

Our findings in the lungs were quite interesting (Fig. 7). There is a radioautographic wreath in the lumina of the alveoli and bronchi. Our study of lung preparations led us to the conviction that an excretion takes place here. We obtained the same pictures after intraperitoneal injection of Congo-red labelled with S^{35}, and also after subcutaneous injection of serum labelled with I^{131}. All these findings clearly show that the lungs belong to the reticuloendothelial system. At the same time, it is important to keep in mind the possibility of radioactive "self-contamination" in the experimental animals.

In the hypophyses, which show a particularly strong accumulation of radioactivity following intracardiac injection or oral administration, a large accumulation of Y^{90} was found in the cells, especially in the nuclei (Fig. 8). This can be explained by the affinity of the rare-earth elements, which yttrium chemically resembles in certain regards, with the nucleic acids, as well as with phosphorus compounds in general. The rare-earth elements form, under physiological pH conditions, insoluble complexes with the nucleic acids.[19] The individual cells of the hypophyses, with their anatomical and functional variations, do not differ from one another in this regard.

In our distribution studies we found a strikingly high accumulation of radioactivity in the pancreas after intraperitoneal

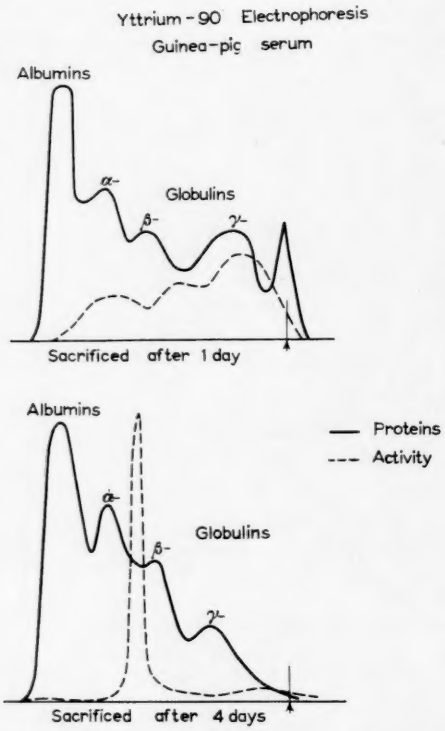


FIG. 14. Electrophoresis of guinea pig serum.

injections. By means of radioautography, differences in accumulation can be shown in this organ, depending on the method of administration. Twenty-four hours after oral administration or intracardiac injection uniform radioautography can be demonstrated throughout the entire section, but after intraperitoneal injection there is, to a certain extent, a gradual permeation from the outside. In the survey given in Fig. 9, which especially shows an interlobular section from the pancreas, a particularly clear accumulation of yttrium can be recognized in the border zone. An enlargement (1200×) of a section in the vicinity of such a deposit plaque (Fig. 10) reveals a concentration of yttrium in individual cell elements in the adipose tissue area. But one can also find a more or less diffuse distribution, becoming stronger in the border areas, throughout the entire pancreas with the exception of the islands of Langerhans.

The ovary showed strong radioautography after intracardiac injection, extending throughout the section and particularly noticeable in the cell nuclei. Fig. 11 shows a part of the antrum folliculi with follicle epithelium.

In the testis a clear concentration of radioactivity in the border zones (Fig. 12), similar to that in the pancreas, can be seen soon after intraperitoneal injection, but later it changes into a diffuse distribution throughout the whole organ. Intracardiac injection immediately produces a diffuse distribution.

A survey of these findings thus shows no essential radioautographical differences in the various methods of administration; rather the variations in distribution seem to be caused by the form of transport.

4. Electrophoretic examinations

We had at our disposal two methods of analysing serum protein and organ protein, and the association of yttrium with certain components of the serum: paper electrophoreses,[20] and starch electrophoreses.[21] In order to trace the processes of kinetic reactions, e.g. during traversal electrophoreses, we constructed an electrophoreses chamber with a built-in Geiger counter (Fig. 13).

The serum pherogram, with subsequent registration of the radioactivity curve, is the same for all methods of administration, but it shows a different curve pattern after 24 hr and after 4 days (Fig. 14). The pherogram of serum 24 hr after administration shows a strong similarity between the curve pattern of Y^{90}-radioactivity and the curve pattern of stained sudanophil substances (mainly lipids). After 4 days the picture is completely different: here we find an activity peak lying between the α- and β-globulins. In the electrophoreses of organ homogenization we obtained in each case an activity peak lying above the point where the serum was applied to the paper, i.e. an yttrium factor is present which does not migrate in paper electrophoreses.

By means of starch electrophoreses we were able to separate the Y^{90} contained in the serum into two fractions: the first

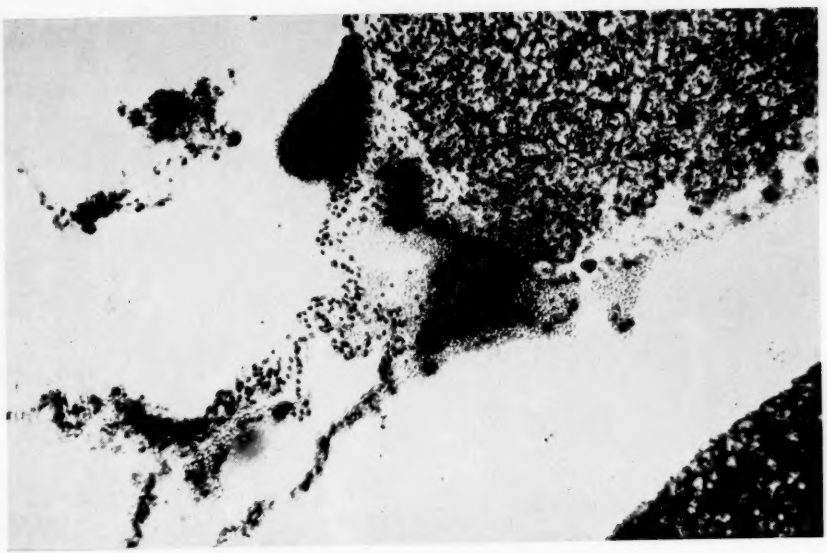
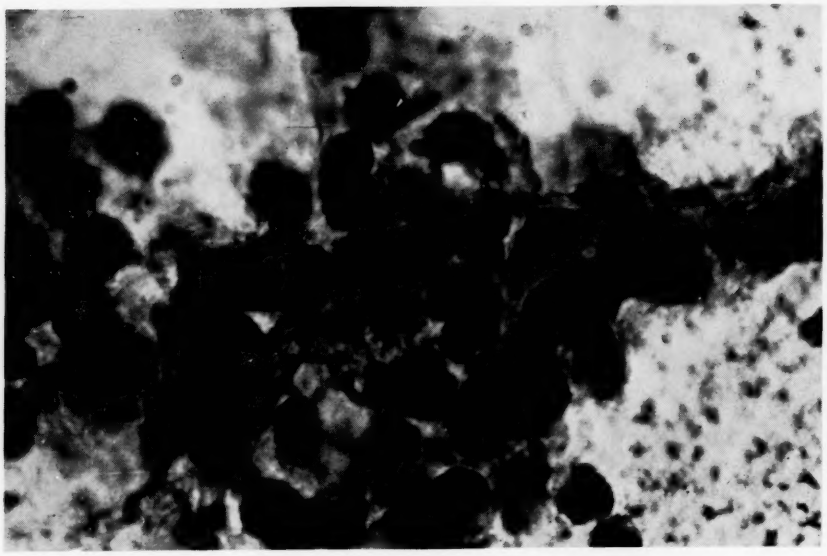


FIG. 9. Radioautography: Pancreas, border zone with adipose tissue (×250).



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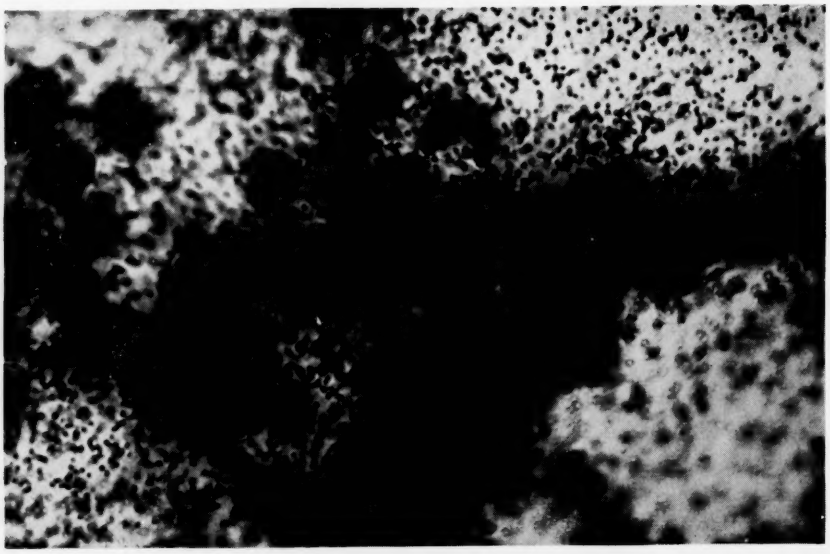

(b)

FIG. 10. Radioautography: Adipose and connective tissue on the border of the pancreas.
(a) Histology, (b) Radioautography.
Enlargement of Fig. 9.

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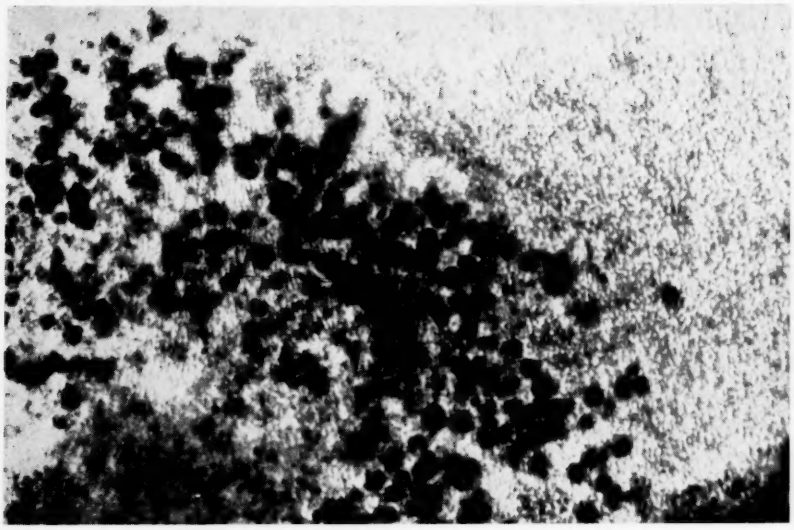

FIG. 11. Radioautography: Ovary, section of the antrum folliculi × 250.

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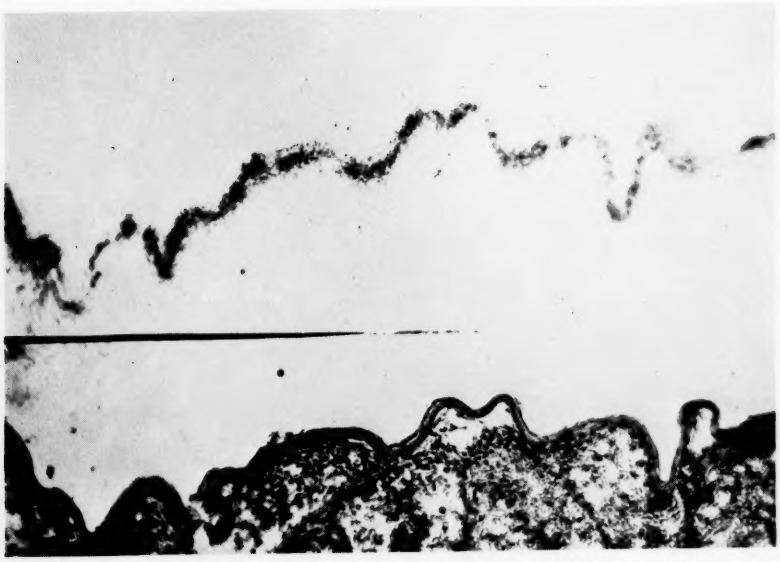

FIG. 12. Radioautography: Testicle capsule (×250).

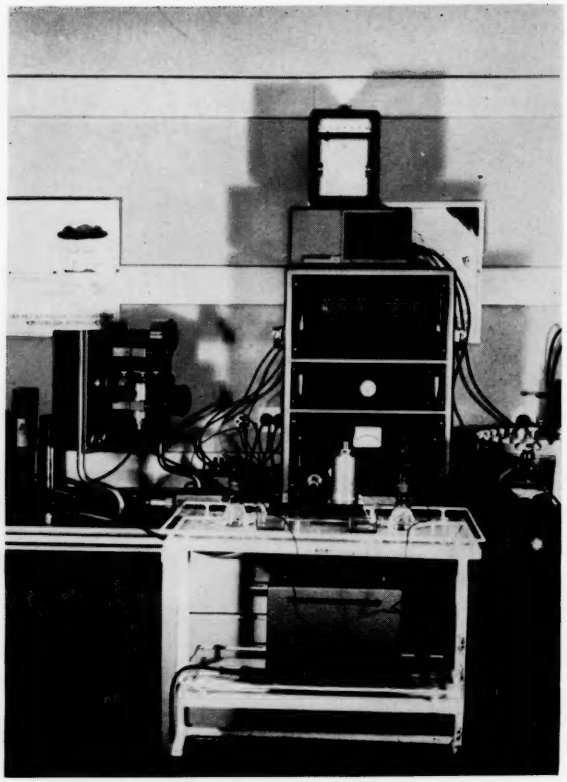

FIG. 13. Electrophoresis chamber with built-in Geiger counter.

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remains at the place of application and corresponds to a colloidal form of yttrium similar to that in organ electrophoreses; the second fraction migrates in front of the albumins.

On the assumption that Y^{90} might have a connexion with the lipoids, we extracted fat from serum, pancreas, adipose tissue, and liver; the lipoids were divided into three subfractions: phospholipoids, cholesterin, and neutral fatty acids.

Of these, the phospholipoids clearly show the highest specific radioactivity (Table 4).

TABLE 4. Lipid extraction: Specific activity in %

Source	Phospholipoids	Cholesterin	Fatty acids
Serum	70	22	6
Pancreas	77	23	1
Adipose tissue	70	27	6
Liver	80	9	7

Here it must be mentioned that, in adipose tissue for example, only 0·1–1·0 per cent of the specific radioactivity remains in the extract; the remaining percentages are residual. In the case of the liver the figure is 10–20 per cent, i.e. considerably higher; this is undoubtedly due to a relation with the phospholipoids present in the organs.

5. Discussion of the results

In surveying the whole complex of our examination results, we see that Y^{90} can by no means be called a "bone seeker" during the first 8 days, a period which is of great radiobiological importance. Within this period we never find more than 30 per cent of the dose in the skeletal system. On the other hand, there are high specific activities, depending on the method of administration, in the metabolically important organs, such as the pancreas, the hypophyses, and also in the genitals. The radioautographical pictures show that the variations in distribution are the result of the different transport mechanisms. Thus we assume that after intraperitoneal injection transport takes place mainly by way of the lymph. Furthermore, radioautography makes clear the formation of complexes on the part of yttrium and the nucleic acids; the relation between yttrium and the phospholipoids is also confirmed by a closer examination of the individual lipid fractions.

From the point of view of radioactive contamination, the accumulation of Y^{90} in the genitals, especially the ovaries, is important. The excretion of the radioisotope which we found in the lung seems to us important in so far as the lung is shown to function as an organ of the reticuloendothelial system; furthermore, the possibility of recontamination in animal experiments must be kept in mind.

Thus our distribution studies of Y^{90} produced results which are not only important in the question of incorporation–decorporation, but which also point to further medical and biochemical problems.

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The Effectiveness of Oral Ammonium Chloride on Increased Excretion of Radio-strontium in Man*†

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The hazard of contamination of the human body by Sr^{90} has become a very important medical problem. This report deals with the effectiveness of oral ammonium chloride as an agent capable of decreasing body retention of radio-strontium.

Strontium-85 was used in these experiments because it is considerably less hazardous than Sr^{90}. Both isotopes share a similar metabolic pattern of behavior.

Two patients were studied. One was a 61 year old negro (Patient A) who had had polyneuritis, malnutrition and mild osteoporosis. He was much improved and ambulatory at the time of these studies. The other patient was a 62 year old white man (Patient B) who had Paget's disease. Both were maintained on a low calcium diet (150 mg a day) on the metabolic ward.

In the control study, an intravenous dose of Sr^{85} was administered. Blood, urine and stool specimens at regular intervals were studied for radioactivity in a scintillation counter. Following at an interval, a second study was commenced. In this study 9 g of ammonium chloride in the form of enteric coated tablets were given 1 day prior to administration of the isotope and for 8 days thereafter.

In the control study, Patient A excreted in urine 7·8 per cent of the administered dose of the isotope within 24 hr and 32·4 per cent at the end of 14 days. Plasma levels dropped sharply during the first hour following Sr^{85} injection and then declined gradually. Total stool excretion at the end of 14 days was 13·5 per cent. When the patient was given ammonium chloride, his urine contained 14·7 per cent of the administered dose of the isotope in the first 24 hr and 62·3 per cent by the end of the 14th day. Disappearance rate of strontium from plasma was steeper than in the control study. Stool excretion amounted to 11·5 per cent. Hence, with ammonium chloride only 26·2 per cent of the administered dose remained in body tissues as compared to 54·1 per cent in the control study. There was also a very striking increase in calcium excretion in the urine in this latter study.

Patient B excreted in urine 4 per cent of the administered dose of the isotope within 24 hr and 13·9 per cent at the end of 12 days. Plasma levels of isotope were lower than that of Patient A by 2-fold. Stool contained 7·4 per cent of the dose. When ammonium chloride was given, this patient excreted in urine 8·4 per cent of the administered dose of Sr^{85} within 24 hr and 38·3 per cent at the end of 12 days. A striking enhancement in urinary calcium was also found in this patient when ammonium chloride was given. Total stool excretion amounted to 8·2 per cent. Hence, with ammonium chloride administration only 54·5 per cent of the administered dose remained in body tissues as compared to 78·7 per cent in the control study.

* This paper is dedicated to the memory of Daniel Laszlo, M.D. He was a Clinician, Investigator, Teacher and Humanitarian of the Old Tradition.

† This work was conducted under Contract AT 30–1 (1763) Atomic Energy Commission.

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This avidity for Sr^{85} demonstrated in this patient paralleled a similar avidity for calcium. This had been demonstrated prior to these studies by low urinary calcium excretion levels and by retention of a large percentage of a given intravenous test dose of calcium gluconate.

When it was discovered that the enteric coated ammonium chloride tablets were responsible for a very large stool excretion of calcium, a third study was carried out using ammonium chloride tablets containing only very small amounts of calcium. Again a very striking enhancement of Sr^{85} and calcium excretion was observed to occur.

It is believed that the effectiveness of ammonium chloride in reducing body retention of Sr^{85} results from the metabolic acidosis which mobilizes skeletal calcium and increases renal excretion of calcium and Sr^{85}. In this manner skeletal deposition of the radio-strontium is decreased.

Emphasis is given to the fact that enhancement of Sr^{85} excretion was favored by the early administration of ammonium chloride following a dose of Sr^{85}. That is, when the plasma and soft tissue concentration of this radioactive element were highest and when it was not yet firmly lodged in the skeleton.

L'EFFICACITÉ DU CHLORURE D'AMMONIUM PRIS PAR LA BOUCHE POUR AUGMENTER L'EXCRÉTION DU RADIO-STRONTIUM CHEZ L'HOMME

Le hasard de la contamination du corps humain par le Sr^{90} est devenu un problème médical de haute importance. Cette communication traite de l'efficacité du chlorure d'ammonium pris par la bouche comme agent capable de diminuer la rétention du radio-strontium dans le corps.

Le Sr^{85} fut employé dans ces expériences parce que son emploi comporte bien moins de danger que celui du Sr^{90}. Les deux isotopes ont des comportements métaboliques pareils.

Deux malades furent étudiés. L'un, un nègre âgé de 61 ans (Malade A) avait souffert de la polynévrite, de nutrition défectueuse et de l'osteoporose tempérée. Sa condition était beaucoup améliorée, il était ambulant à l'époque de ces études. L'autre malade était un blanc âgé de 62 ans (Malade B) ayant la maladie de Paget. Tous deux étaient tenus à un régime pauvre en calcium (150 mg par jour) dans la salle métabolique.

Dans l'expérience de contrôle, une dose intraveineuse de Sr^{85} fut administrée. Des échantillons de sang, d'urine et de selles pris à des intervalles réguliers furent examinés pour la radio-activité dans un compteur à scintillation. Après une période, une deuxième expérience fut commencée. Dans celle-ci, 9 g de chlorure d'ammonium formé en comprimés kératinisés furent donnés un jour avant l'administration de l'isotope et pendant les 8 jours suivant.

Dans l'expérience de contrôle, Malade A excréta dans l'urine 7,8 pour cent de la dose d'isotope administrée, dans 24 hr, et 32,4 pour cent au bout de 14 jours. Les niveaux dans le plasma diminuèrent abruptement dans la première heure suivant l'injection du Sr^{85} et puis alors diminuèrent graduellement. Le totale excrété dans les selles au bout de 14 jours fut 13,5 pour cent. Lorsque le malade recevait le chlorure d'ammonium, son urine contenait 14,7 pour cent de la dose d'isotope administrée dans les premières 24 hr et 62,3 pour cent à la fin du 14me jour. Le taux de disparition du strontium hors du plasma fut plus fort que dans l'expérience de contrôle. L'excrétion dans les selles monta à 11,5 pour cent. Ainsi, avec le chlorure d'ammonium seulement 26,2 pour cent de la dose administrée restait dans les tissus du corps, comparé à 54,1 pour cent dans le contrôle. Il y avait aussi dans cette expérience une augmentation très marquée dans l'excrétion de calcium dans l'urine.

Malade B excréta dans l'urine 4 pour cent de la dose administrée dans 24 hr et 13,9 pour cent au bout de 12 jours. Les niveaux d'isotope dans le plasma furent inférieurs à ceux du Malade A par 2 fois. Les selles contenaient 7,4 pour cent de la dose. Lorsque fut donné le chlorure d'ammonium, ce malade excréta dans l'urine 8,4 pour cent de la dose de Sr^{85} administrée dans 24 hr et 38,3 pour cent à la fin de 12 jours. Une augmentation remarquable de calcium urinaire fut aussi observée chez ce malade lors de l'administration du chlorure d'ammonium. Le totale excrété dans les selles monta à 8,2 pour cent. Donc, lors de l'administration du chlorure d'ammonium seulement 54,5 pour cent de la dose administrée restait dans les tissus du corps comparé à 78,7 pour cent dans le contrôle. Cette avidité pour le Sr^{85} que montra ce malade fut appareillée par une avidité semblable pour le calcium. Ceci

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avait été montré antérieurement à ces recherches par des niveaux peu élevés d'excrétion urinaire de calcium et par la rétention d'une grande proportion d'une dose épreuve de gluconate de calcium donnée intraveineusement.

Lors de la découverte que les comprimés de chlorure d'ammonium kératinisés produisaient une très forte excrétion de calcium dans les selles, une troisième expérience fut achevée utilisant des comprimés de chlorure d'ammonium ne contenant que de très petites quantités de calcium. Encore se fit observer une augmentation très marquée de l'excrétion du Sr^{85} et du calcium.

On croit que l'efficacité du chlorure d'ammonium en diminuant la rétention du Sr^{85} dans le corps vient de l'acidose métabolique qui mobilise le calcium squelettique et augmente l'excrétion rénale du calcium et du Sr^{85}. De cette façon se diminue la déposition squelettique du radio-strontium.

On accentue le fait que l'amélioration de l'excrétion du Sr^{85} fut favorisée par l'administration rapide du chlorure d'ammonium suivant la dose de Sr^{85}; c'est-à-dire, quand les concentrations de cet élément radioactif dans le plasma et dans le tissu mou étaient au maximum et quand il n'était pas encore déposé rigidement dans le squelette.

ВЛИЯНИЕ ПРИНИМАЕМОГО ВНУТРЬ ХЛОРИСТОГО АММОНИЯ НА УВЕЛИЧЕНИЕ ВЫВЕДЕНИЯ РАДИОСТРОНЦИЯ С КАЛОМ ЧЕЛОВЕКА

Опасность заражения человеческого организма Sr^{90} становится очень актуальной медицинской проблемой. В данной статье рассматривается эффективность принимаемого внутрь хлористого аммония, как агента, способствующего уменьшению задержания радиостронция организмом.

В опытах применялся Sr^{85}, так как он значительно менее опасен, чем Sr^{90}. Метаболическое поведение обоих изотопов одинаково.

Исследованию были подвергнуты 2 пациента. Один 60-летний негр (пациент А) пониженного питания, страдающий полиневритом и остеопорозом в легкой форме. После экспериментов ему стало гораздо лучше и он получил возможность двигаться. У второго пациента 62-летнего белого (пациент В) была болезнь Пэджета. Оба были помещены в метаболическую палату и посажены на диету с малым содержанием кальция (150 мг в день).

В контрольном опыте доза Sr^{85} вводилась внутривенно. Кровь, моча и кал проверялись на радиоактивность через определенные промежутки времени при помощи сцинтилляционного счетчика. Через некоторое время было начато второе исследование, при котором больному давали 9 г хлористого аммония в таблетках, растворяющихся только в тонких кишках, за день до и через 8 дней после введения изотопа.

В контрольном опыте у пациента А 7,8% введенной дозы изотопа были выведены с мочей за первые 24 часа, 32,4% по истечении 14 дней. Содержание изотопа в плазме резко упало в течение первого часа вслед за инъекцией Sr^{85}, а затем стало уменьшаться постепенно. Общее количество изотопа, выведенного с калом за 14 дней, составило 13,5%. При принятии пациентом хлористого аммония 14,7% введенной дозы изотопа было выведено за 24 часа, 62,3% по истечении 14 дней. Скорость выведения стронция из плазмы увеличивалась резче, чем в контрольном опыте. Выведение с калом составляло 11,5%. Таким образом при применении хлористого аммония в тканях тела задерживалось только 26,2% введенной дозы изотопа, по сравнению с 54,1% в контрольном опыте. Выведение кальция с мочей также резко увеличилось в последнем опыте.

У пациента В 4% введенной дозы изотопа было выведено с мочей за 24 часа, 13,9% по истечении 12 дней. Концентрация изотопа в плазме была вдвое ниже, чем у пациента А. Кал содержал 7,4% дозы. Когда пациент принимал хлористый аммоний 8,4% введенной дозы Sr^{85} были выведены с мочей за первые 24 часа, 38,3% по истечении 12 дней. Хлористый аммоний привел также к резкому увеличению кальция в моче. С калом было выведено всего 8,2%. Таким образом при применении хлористого аммония в тканях тела задерживалось только 54,5% введенной дозы, по сравнению с 78,7% в контрольном опыте. Организм данного пациента имеет тенденцию усиленно поглощать как Sr^{85}, так и кальций. Об этом можно было судить еще до начала опытов по низкому уровню выведения кальция с мочей и большому проценту задержания кальций глюконата, вводимого внутривенно.

После того как было показано, что таблетки хлористого аммония, растворяющиеся только в тонких кишках, ответственны за высокий процент выведения кальция с калом, был поставлен третий опыт с применением таблеток с низким содержанием кальция. Выведение Sr^{85} и кальция снова резко увеличилось.

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Предполагается, что эффективность хлористого аммония в отношении уменьшения задержания Sr^{85} в тканях тела обуславливается обменным ацидозом, который мобилизует кальций, находящийся в костях и увеличивает выведение кальция почками. Таким образом уменьшается отложение радиостронция в костных тканях.

Подчеркивается тот факт, что усиленному выведению Sr^{85} способствует инъекция хлористого аммония вслед за принятием Sr^{85}, т.е. тогда, когда концентрация радиоактивного элемента в плазме и тканях является наивысшей и когда изотоп еще не успел укрепиться в костных тканях.

DIE WIRKSAMKEIT VON ORALEM AMMONCHLORID AUF DIE GESTEIGERTE RADIOSTRONTIUM-AUSSCHEIDUNG IM MENSCHEN

Die Gefährdung durch die Verseuchung des menschlichen Körpers mit Sr^{90} ist zu einem sehr wichtigen medizinischen Problem geworden. Dieser Bericht behandelt die Wirksamkeit von oralem Ammoniumchlorid als geeignetes Mittel zur Herabsetzung der Retention von Radiostrontium in Körper.

Für diese Versuche wurde Sr^{85} verwendet, da dieses für bedeutend weniger gefährlich als Sr^{90} angesehen wird. Beide Isotopen zeigen bezüglich Stoffwechsels das gleiche Verhalten. Zwei Patienten wurden untersucht. Einer davon, ein 61-jähriger Neger (Patient A) litt an Polyneuritis, Unterernährung und leichter Osteoporose. Sein Zustand war zum Zeitpunkt der Untersuchung bereits sehr gebessert und er war ambulant. Der andere Patient war ein 62-jähriger Weisser (Patient B) mit Paget-Erkrankung. Beide wurden auf niedriger Kalziumdiät gehalten (150 mg pro Tag) und befanden sich in der Abteilung für Stoffwechseluntersuchungen. Beim Kontrollversuch wurde eine intravenöse Dosis Sr^{85} verabreicht. Blut-, Urin- und Stuhlproben wurden in regelmässigen intervallen bezüglich ihrer Radioaktivität mit Hilfe ein Szintillationszählers untersucht. Nach Ablauf einer bestimmten Zeit wurde mit einer zweiten Untersuchung begonnen, dabei wurden 9 g Ammonchlorid in Form von im Dünndarm löslichen Tabletten einen Tag vor und 8 Tage nach der Isotopengabe verabreicht.

Beim Kontrollversuch waren vom Patient A im Urin 7,8 Prozent der verabreichten Strontium-Dosis innerhalb von 24 Stunden ausgeschieworden und 32,4 Prozent nach Ablauf von 14 Tagen. Der Gehalt im Plasma fiel während der 1. Stunde nach der Injektion scharf, später langsamer ab. Die gesamte Ausscheidung durch den Stuhl betrug am Ende von 14 Tagen 13,5 Prozent. Nach Gabe von Ammoniumchlorid enthielt sein Urin 14,7 Prozent der verabreichten Strontium-Dosis innerhalb der ersten 24 Stunden und 62,3 Prozent nach Ablauf von 14 Tagen. Die Clearance-Rate von Strontium im Plasma war steiler als beim Kontrollversuch. Auf Stuhlausscheidung entfielen 11,5 Prozent. Dies bedeutet, dass mit Ammoniumchlorid nur 26,2 Prozent der verabreichten Dosis im Körpergewebe verbleiben, verglichen mit den 54,1 Prozent beim Kontrollversuch. Ausserdem zeigte sich in diesem Falle auch auffallende Zunahme der Ca-Ausscheidung im Urin.

Beim Patienten B wurden im Urin 4 Prozent der verabreichten Isotopen-Dosis innerhalb von 24 Stunden und 13,9 Prozent im Ablauf von 12 Tagen ausgeschieden. Der Strontiumgehalt des Plasmas betrug nur die Hälfte des Wertes vom Patienten A. Der Stuhl enthielt 7,4 Prozent der Dosis. Nach Anwendung vom Ammoniumchlorid wurde von diesem Patienten im Urin 8,39 Prozent der Sr^{85}-Dosis innerhalb von 24 Stunden und 37,26 Prozent nach Ablauf von 12 Tagen ausgeschieden. Auch hier bewirkte das Ammoniumchlorid eine auffallende Zunahme des Calciums im Harn. Die totale Ausscheidung mit dem Stuhl stieg auf 8,4 Prozent. Die Ammoniumchloridgabe bewirkte daher bei diesem Patienten, dass nur 54,5 Prozent des verabreichten Strontiums im Körper verblieben, verglichen mit 78,7 Prozent beim Kontrollversuch. Die gesteigerte Strontiumaufnahmebereitschaft dieses Patienten entsprach einer gleichartigen Aufnahmebereitschaft für Calcium. Dies war bereits vor den beschriebenen Versuchen durch eine niedrige Ca-Ausscheidung im Harn und durch die Retention eines grossen Prozentsatzes von intravenösem Ca-Gluconat gezeigt worden. Als sich herausstellte, dass die dünndarmlöslichen Ammoniumchlorid-Tabletten für eine sehr starke Ca-Ausscheidung im Stuhl verantwortlich waren, wurde eine dritte Versuchsreihe angesetzt, wobei Ammoniumchlorid-Tabletten mit nur sehr geringem Ca-Gehalt verwendet wurden. Es wurde abermals ein augenfälliger Anstieg der Sr^{85}-Ca-Ausscheidung beobachtet. Es wird angenommen, dass die Wirksamkeit des Ammoniumchlorides bei der Herabsetzung der Retention von Sr^{85} auf der Stoffwechselacidose

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beruht, welche Ca aus dem Skelett mobilisiert und die Ausscheidung von Ca und Sr^{85} auf dem Nierenwege verstärkt. Auf diese Weise wird die Ablagerung von Radio-Strontium in den Knochen herabgesetzt.

Es sei betont, dass die Steigerung der Sr^{85}-Ausscheidung dann besonders gross sein wird, wenn die Gabe von Ammoniumchlorid möglichst bald auf die Verabreichung von Sr^{85} erfolgt, das heisst, wenn die Konzentration dieses radioaktiven Elementes im weichen Gewebe besonders gross ist und noch keine Fixierung im Knochen stattgefunden hat.

INTRODUCTION

THE hazard of contamination of the human body by Sr^{90} has become a very important medical problem. The source of contamination may be either fallout due to nuclear fission or overexposure to this radioactive element in research or in an industrial plant.

The ill effects resulting from internal radiation of Sr^{90} in experimental animals are well documented in the literature.[1–11] With the increased possibilities of overexposure to this element, it would indeed be important to have available methods and means of decontaminating the human body of this radioactive element as quickly and completely as possible.

This report deals with the effectiveness of oral ammonium chloride as an agent capable of decreasing body retention of radio-strontium.

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MATERIALS AND METHODS

Strontium-85 was used in these studies because it is considerably less hazardous than Sr^{90}. Although both isotopes share a similar metabolic pattern of behavior, Sr^{85} is a γ-emitter (0·51 MeV) with a half-life of only 65 days compared to Sr^{90}, a β-emitter with a half-life of 25 years. Strontium-85 is produced by cyclotron bombardment of Rb^{85}.

Study I in each patient was a control study. Following at an interval Study II consisted of observations during administration of ammonium chloride. Both patients were given 9 g of ammonium chloride (0·5g enteric coated tablets) in three divided doses one day prior to administration of the isotope and for eight days thereafter. This regimen was discontinued when carbon dioxide determination indicated that both patients were acidotic. Periodic determinations were made on serum carbon dioxide, chloride, sodium, potassium and calcium. Daily urinary calcium and phosphorus determinations were made prior to and during these studies. Determinations for calcium and phosphorus in stools were made on specimens separated by markers and pooled during each six-day metabolic period. Calcium determinations were made on ashed specimens of acidified urine and stool by oxalate precipitation. Serum calcium was determined by Collipp modification of the Cramer–Tysdale method.

Two patients were studied on the metabolic ward. Patient A was a 61 year old Negro man who had polyneuritis, malnutrition, and mild osteoporosis. At the time of these studies he was much improved and ambulatory. Patient B was a 62 year old white man who had Paget's disease. Both patients had been on a low calcium diet (150 mg calcium a day) for two metabolic periods. The patients were maintained on this metabolic regimen throughout the studies and during interim periods between the studies.

In Study I, Patient A was injected with approximately 6 μc of Sr^{85}. The study lasted fourteen days. Twenty-two days after the conclusion of Study I, the patient was given an intravenous dose of 4·5 μc. This study also lasted fourteen days.

A dose of approximately 6·3 μc of Sr^{85} was given Patient B in Study I, which

lasted twelve days. In Study II started 69 days after the completion of Study I, a dose of 4·5 μc was administered intravenously. This study also lasted for twelve days.

Strontium-85 was administered intravenously in the following manner: An infusion of 290 ml isotonic saline was allowed to run for a period of exactly 1 hr. At the midpoint of the infusion, the isotope was injected directly through the distal portion of the tubing, the proximal portion of the tubing being clamped to prevent reflux of the isotope into the infusion bottle. The flow of the solution was then restarted, the injecting syringe was withdrawn and the remainder of the infusion was completed.

Blood specimens were drawn 5 min, 1 hr, 4 hr, 8 hr and 24 hr after injection of the isotope and every 24 hr thereafter. Stool specimens were collected daily and were homogenized with a known quantity of water and weighed aliquots of about 5 g were placed into test tubes and the radioactivity was determined. Blood specimens were centrifuged and 2–5 ml of plasma were removed for determination of radioactivity. Urine collections were measured for total volume, then acidified and 5 ml samples were pipetted into test tubes for determination of radioactivity. All samples were counted in a scintillation counter with an average background of radioactivity of 135–140 counts per min.

Calcium balances of Study II of both patients revealed calcium in stool far in excess of the dietary calcium intake. For instance, the stool excretion of Patient A during the period of calcium administration was 1036 mg a day. When the ammonium chloride enteric coated tablets were analyzed to ascertain whether they were responsible for the additional calcium intake, it was found that each tablet contained 40 mg of calcium or 720 mg calcium in the 18 tablets, which were administered daily. Study III was performed on this patient nine days after completion of Study II, using ammonium chloride tablets* containing only 7 mg of calcium per 1 g tablet or a total of only 63 mg calcium a day.

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OBSERVATIONS

In Study I, the control, osteoporotic Patient A excreted in the urine during the first 24 hr 7·8 per cent of the administered dose of Sr^{85} (Table 1 and Fig. 1). Thereafter, a steady decline in radioisotope loss each day was noted until the values approximated that of the background radioactivity by the fourteenth day. Plasma levels dropped sharply during the first hour following Sr^{85} injection and then declined gradually. The stool obtained during the first 24 hr contained a trace of radioactivity. The 24 hr urinary calcium excretion ranged between 49 and 99 mg (Fig 1). At the end of 14 days, the patient had excreted 32·4 per cent of the administered dose of isotope in the urine; 13·5 per cent in the feces or a total of 45·9 per cent. Hence 54·1 per cent of the dose remained in the body. When the patient was given ammonium chloride (Study II), 14·7 per cent of the administered dose of Sr^{85} was excreted in the urine during the first 24 hr and there is, compared to Study I, a very striking and sustained enhancement of strontium excretion during the period of ammonium chloride administration and for a few days thereafter (Table 1, Fig. 1). Concomitant with this very striking increase in strontium excretion, there was a striking increase in urinary calcium excretion, which started on the first day of ammonium chloride administration and continued rising steeply during the subsequent days of this regimen. When ammonium chloride was discontinued, there was initially a sharp drop of the urinary calcium output with a steady decline subsequently. Urinary phosphorus excretion did not appear to follow any particular pattern of behavior and for this reason these figures are omitted.

The disappearance rate of strontium from

* Amchor, enteric coated 1g tablets—Brewer and Company.

TABLE 1. The effect of oral ammonium chloride on radio-strontium excretion in Patient A

Day		Strontium-85 in plasma (% dose)			Strontium-85 in urine (% dose)			Calciuria (mg/24 hr)		
		I*	II†	III‡	I	II	III	I	II	III
								Prestudy	59 60	34 33
									116 ↑	73 ↑
1	5 min	21·83	19·6	25·06						
	1 hr	9·30	10·5	10·49						
	4 hr	7·87	8·00	8·19						
	8 hr	5·39	5·70	6·81						
	24 hr	4·34	4·50	4·94	7·81	14·72	9·85	95	168	104
2		–	–	–	4·46	9·49	7·64	49	230	131
3		3·07	3·28	3·50	3·80	9·01	7·61	86	327	212
4		2·33	2·54	2·82	2·80	6·51	5·40	77	362	223
5		1·82	1·73	1·80	2·30	4·72	4·77	78	330	245
6		1·63	1·61	1·66	1·91	3·31	4·57	80	298	310 ↓
7		–	1·04	1·30	1·67	4·10	2·63	83	453	197
8		1·10	0·69	1·00	1·58	3·14	2·29	87	434 ↓	192
9		1·05	–	–	1·31	2·13	1·59	78	296	142
10		1·00	0·40	0·76	0·95	1·37	1·36	58	214	135
11		–	–	0·63	1·16	1·16	1·20	90	190	116
12		0·83	0·26	–	1·10	0·83	–	99	138	–
13		–	–	0·58	0·85	0·99	0·67	89	176	78
14		0·76	0·40	–	0·65	0·85	0·55	75	161	66
				Total:	32·35	62·33	50·13			

9 g NH_4Cl a day

* 6 μc of Sr^{85} administered intravenously on 6 February 1956.
† 4·5 μc of Sr^{85} administered intravenously on 14 March 1956.
‡ 6 μc of Sr^{85} administered intravenously on 6 April 1956.
N.B. Cumulative Sr^{85} excretion in stool: Study I: 13·5% in 14 days. Study II: 11·5% in 14 days.
Study I : Low calcium intake.
Study II : High calcium intake.
Study III: Low calcium diet plus 65 mg/day excess.

plasma in Study II was steeper than in Study I. There was no significant difference in fecal Sr^{85} in the two studies. At the end of day 14 when ammonium chloride was given, 62·3 per cent of the administered dose of isotope had been excreted in the urine as compared to only 32·4 per cent in the control study. With stool excretion of 11·5 per cent only 26·2 per cent remained in body tissues as compared to 54·6 per cent in the control study (Fig. 1).

Patient B, who had Paget's disease, excreted less Sr^{85} in the urine during the first 24 hr as well as on subsequent days during the control study (Study I, Table 2 and Fig. 2). During the first 24 hr, he excreted 4·0 per cent of the administered dose of isotope in the urine. Plasma levels of isotope are lower than that of Patient A by two-fold. Of the administered dose of Sr^{85}, 7·4 per cent was excreted in the stool in the control study at the end of twelve days. Daily urinary calcium excretion remained constant ranging between 40 and 50 mg.

Under the influence of ammonium chloride, this patient excreted 9·4 per cent of the strontium in the urine during the first 24 hr. Thereafter the enhancement was even greater than two-fold; on some days as much as three to six times the amount of radio-strontium excreted in the control study (Table 2). By the twelfth day only 54·5 per cent of the isotope remained in the body in Study II compared to 78·7 per cent in Study I (Fig. 2). Along with the

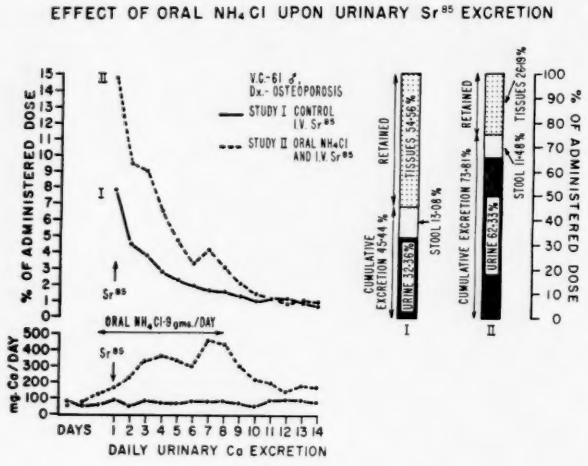

FIG. 1. This graph indicates the striking enhancement of Sr^{85} excretion in the urine of Patient A caused by oral ammonium chloride. The patient is a 61 year old Negro male with osteoporosis. During Study I he was kept on a low calcium diet. In Study II he was given 9 g a day of ammonium chloride by mouth. The graph indicates that at the end of 14 days while on ammonium chloride, 62·33 per cent of the administered dose of Sr^{85} was excreted in the urine as compared to only 32·36 per cent of the administered dose in the control study. A very marked increase in calciuria is also noted during the period of ammonium chloride administration.

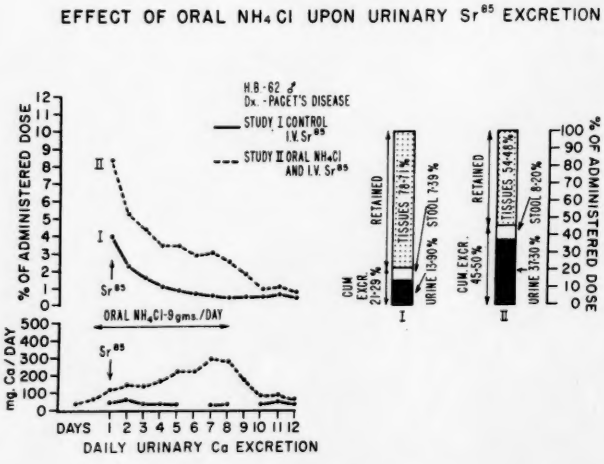

FIG. 2. Patient B is a 62 year old white man with Paget's disease. This figure indicates the striking enhancement of Sr^{85} excretion in the urine when 9 g of ammonium chloride was given orally. At the end of 12 days, the urinary excretion of Sr^{85} was 37·30 per cent of the administered dose as compared to 21·29 per cent in the control study. Note that more Sr^{85} was retained in the tissues of this patient during both studies than was retained in the tissues of Patient A. This avidity for Sr^{85} was paralleled by a similar avidity for calcium given intravenously. A very marked increase in calciuria is also demonstrated during the period of ammonium chloride administration.

marked increase in urinary Sr^{85} excretion, there was also a marked increase in urinary calcium output.

In Study III, Patient A excreted 9·9 per cent of the administered dose in urine during the first 24 hr (Table 1). At the conclusion of this study (day 13) a total of 49·6 per cent of the radio-strontium was excreted in urine. The decline of isotope levels in plasma was not significantly different from that of the previously described studies. During the 3 days prior to ammonium chloride administration, the urinary calcium excretion ranged between 33 and 41 mg a day. During the 8 days of ammonium chloride administration, the daily urinary calcium output ranged between 73 and 310 mg. Stool strontium excretion was similar to the output in Studies I and II of this patient.

DISCUSSION

Decalcification of skeleton following the administration of ammonium chloride is a phenomenon that has been known for a long time. Indeed, early clinicians harnessed this effect of ammonium chloride by therapeutically decalcifying skeleton to help correct bone deformities due to rickets.

In 1924, BERNHARDT[12] established the

TABLE 2. The effect of oral ammonium chloride on radio-strontium excretion in patient B

Day		Strontium-85 in plasma (% dose) I*	Strontium-85 in plasma (% dose) II†	Strontium-85 in urine (% dose) I	Strontium-85 in urine (% dose) II	Calciuria (mg/24 hr) I	Calciuria (mg/24 hr) II	
							34	Prestudy
							40	Prestudy
							67	↑
1	5 min	–	12·5					
	1 hr	6·49	7·04					
	4 hr	4·32	4·44					
	8 hr	3·22	3·35					
	24 hr	1·93	2·14	4·00	8·39	40	115	9g NH_4Cl a day
2		–	–	2·32	5·28	51	146	
3		1·79	1·69	1·60	4·41	42	135	
4		1·11	1·51	1·19	3·51	34	167	
5		0·82	0·97	0·90	3·48	37	222	
6		0·80	0·85	0·74	2·94	–	224	
7		0·73	0·70	0·59	3·09	34	289	
8		–	0·45	0·48	2·58	29	279	↓
9		0·60	–	0·50	1·80	–	173	
10		–	0·61	0·50	0·92	31	83	
11		–	–	0·63	1·09	45	89	
12		–	0·46	0·45	0·77	34	54	
			Total:	13·90	38·26			

* 6·3 μc of Sr^{85} administered intravenously on 11 January 1956.
† 4·5 μc of Sr^{85} administered intravenously on 13 March 1956.
N.B. Cumulative Sr^{85} excretion in stool: Study I: 7·4% in 12 days. Study II: 8·2% in 12 days.
Study I : Low calcium intake.
Study II: High calcium intake.

fact that there was increased calcium and phosphorus excretion especially via the kidneys as a result of the metabolic acidosis which occurs when HCl is liberated with the synthesis of urea from the ammonium radicle. Later, ALBRIGHT *et al.*[13] studying the effects of ammonium chloride in humans reported a prompt rise in urinary calcium excretion. JAFFE *et al.*[14] in 1931 were able to produce marked decalcification of the skeletal systems of growing dogs treated with ammonium chloride.

Because of this known effect upon skeletal calcium, ammonium chloride was studied in humans when the problem of radium deposition in bone was of great interest. Using ammonium chloride and parathyroid extract simultaneously, FLINN[15] in 1931 reported enhanced excretion of radium in humans contaminated with this radioactive element. AUB *et al.*,[16] studying the effects of ammonium chloride in humans poisoned with radium, reported a four–eight fold elevation of radium excretion when ammonium chloride was given concomitantly with thyroid extract, parathyroid extract, and magnesium gluconate.

The present studies demonstrate that ammonium chloride causes a very marked and sustained increase in radio-strontium excretion. Indeed, the results with this acidifying salt are very striking when compared with results of earlier studies performed in this laboratory by SPENCER *et al.*[17] and CHARLES *et al.*[18] using intravenous calcium to increase Sr^{85} urinary excretion. In the latter studies, the urinary Sr^{85} excretion was increased by about one and one half times the control excretion during the first 24 hr. Thereafter, unless

additional intravenous injections of calcium gluconate were given, there was no enhancement of urinary strontium excretion. With ammonium chloride, however, although the greatest absolute amount of isotope excretion also occurred during the first 24 hr, the increase in isotope excretion was sustained during the administration of this drug and for a few days after it was discontinued. Hence Patient A excreted in urine and feces almost 60 per cent of administered dose of isotope within the first week with ammonium chloride. This much excretion could be attained with intravenous calcium only after several calcium injections and over a period of 3 weeks.

The enhancement of radio-strontium excretion in the present studies was two–four fold that of the control. Fecal excretion of strontium was not increased and no detectable differences were noted in plasma levels. It is interesting to note that although the effect of ammonium chloride was marked in both patients, the actual amount of strontium retained in the patient with Paget's disease was much greater than in the osteoporotic patient. This greater retention of strontium was paralleled by a pronounced avidity for calcium in this patient as evidenced by a 24 hr urinary calcium excretion of only 30–40 mg and an excessive retention of an intravenously injected standard dose of calcium. This same avidity for strontium and calcium was also observed in a patient with advanced osteoblastic lesions secondary to prostatic carcinoma.

The effectiveness of an attempt to remove a "bone-seeking" radioactive element such as strontium appears to be determined by the period of time allowed to elapse after exposure to the element. Thus, the shorter the time interval between exposure to radio-strontium and attempts to remove this element, the greater is the yield. This principle apparently is not unique to strontium. Aub *et al.*[16] observed that radium excretion proceeded at a far more rapid rate in the acute stages of radium poisoning. This was ascribed to the fact that the radium was loosely held in the early stages, but in the later stages bones held on to the radium more tenaciously. Cohn *et al.*[19] demonstrated that the skeletal uptake of yttrium in rats was significantly reduced when ethylenediaminetetra-acetic acid was administered shortly after administration of yttrium. Charles *et al.*[18] showed that as late as 42 days after exposure to Sr^{85}, intravenously administered calcium caused a significant increase in urinary Sr^{85} excretion. However, the absolute amount was much smaller compared to the amounts excreted when the calcium was given at shorter intervals following Sr^{85} administration.

The excess oral calcium intake in Study II was unforeseen. It raises the question of how much a role this ingested calcium might have played in the enhancement of Sr^{85} excretion. During the period of high calcium intake, Patient A received 1085 mg of calcium. During this same period, 1036 mg of calcium were recovered in stool and 266 mg of calcium were excreted in urine. His average excretion based on pooled urine specimens was approximately 60 mg a day and 400 mg in stool. During this same period, the calcium intake of Patient B was 914 mg. His urinary calcium excretion was 164 mg a day and stool excretion 513 mg a day during this period. His average urinary calcium had been approximately 45 mg a day and 175 mg a day in stool. However, parts of undissolved ammonium chloride tablets were recovered in the stools of this patient. Thus it is felt that at best only a fraction of the oral calcium intake was probably absorbed to enter into endogenous metabolic pathways. Brine and Johnston[20] reported that with an increasing oral calcium intake, the percentage absorbed diminishes, until at an intake of 1000–1199 mg a day, only about 28 per cent was absorbed. Other reports are in general agreement with slightly lower figures.

Indeed, available evidence from previous experimental work suggests that the question to be raised might be: How much greater might the excretion of radio-strontium have been were the patients on a low calcium diet during the ammonium chloride regimen? For instance, Jaffe and Bodansky,[14]

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who administered ammonium chloride solution via stomach tube to puppies, observed that the effects of ammonium chloride were strikingly dependent upon the calcium intake. Dogs receiving an adequate calcium intake and ammonium chloride showed less decalcification than those receiving a low calcium diet with or without ammonium chloride. AUB *et al.*[16] gave to their patients who were poisoned with radium, 12–30 g of ammonium chloride a day and found that less radium was excreted in both urine and stool on high calcium intake than on low calcium intake. CRAVER and SCHLUNDT[21] studied four radioactive (radium) girls, who were placed on 3 weeks of high calcium diet with viosterol, then 3 weeks on low calcium diet plus parathyroid extract and then again on 3 weeks of high calcium intake plus viosterol. Only the last 3 days of each period were analyzed, and it was noted that there was increased radium excretion in all analyses with low calcium diet and parathyroid extract.

Furthermore, when the same amount of ammonium chloride was given to Patient A in the form of tablets, which raised the calcium intake to only 63 mg a day (Study III), a striking increase in urinary Sr^{85} and calcium also occurred. That the magnitude of enhancement in Study III is not so great as in Study II is ascribed to the fact that sufficient time had not been allowed to elapse between the two studies. That is to say, Study III was started during a "refractory period" or a "compensatory period" following the large calcium excretion in Study II. This is suggested by the fact that on the several days preceding the onset of Study III, the daily urinary calcium excretions are one-half to one-third the rate of excretion seen on the several days preceding Study II.

It should be noted, however, that the question just raised involves orally ingested calcium. Results of previous work in this laboratory reported by SPENCER *et al.*[17] and CHARLES *et al.*[18] demonstrated that intravenously administered doses of calcium enhance radio-strontium excretion (and indeed one might even speculate a synergistic effect of intravenous calcium and oral ammonium chloride upon the excretion of strontium in man).

It is therefore felt that the *modus operandi* of the striking increase in radio-strontium excretion is the metabolic acidosis that causes mobilization of skeletal calcium and increased renal excretion thereof.

Conclusions

(1) Orally administered ammonium chloride has been shown to be an effective agent in reducing body retention of intravenously administered Sr^{85} in humans.

(2) It is believed that its effectiveness in reducing body retention of Sr^{85} results from the metabolic acidosis that mobilizes skeletal calcium, and increases renal excretion of calcium and Sr^{85}, thereby decreasing skeletal deposition of radio-strontium.

(3) Enhancement of Sr^{85} excretion was favored by administration of ammonium chloride when the plasma and soft tissue concentrations of this radioactive isotope were highest and when it was not yet firmly lodged in the skeleton.

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Marquage d'Abeilles au Moyen d'or Radioactif

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Des essais de marquage des abeilles butineuses (à l'aide d'Au^{198} mélangé sous forme de suspension colloidale à leur nourriture) ont donné quelques renseignements sur leur comportement:
—rayon de dispersion assez faible (environ 1000 m)
—hétérogénéité de cette dispersion.
Les résultats de l'expérience se sont avérés suffisamment satisfaisants pour qu'on envisage la reprise de ces essais avec des moyens accrus.

A METHOD OF LABELLING WORKER BEES BY MEANS OF A RADIOISOTOPE

Tests on the labelling of worker bees (by mixing Au^{198} in the form of a colloidal suspension with their food) have provided some information on their behaviour:
—fairly small radius of dispersion (about 1000 m)
—heterogeneity of this dispersion.
The results of the experiment have proved sufficiently satisfactory so that further tests are planned with improved means.

МЕТОД МЕЧЕНИЯ ПЧЕЛ-РАБОТНИЦ РАДИОИЗОТОПАМИ

Исследование мечения пчел-работниц (примесью Au^{198} в форме коллоидальной суспензии в ихнюю пищу), дало некоторую информацию о их поведении
—довольно маленький радиус рассеяния (около 1000 м)
—неоднородность этого рассеяния
Результаты этого исследования оказались довольно удачными, поэтому дальнейшие исследования будут производиться улучшенными способами.

MARKIERUNG VON BIENEN MIT HILFE VON RADIOGOLD

Versuche mit Markierung von Arbeitsbienen (die Markierung erfolgte durch Beimengung von Au^{198} in Kolloidal-suspension in das Futter), lieferten die folgenden Informationen über ihr Verhalten:
—sie verteilen sich über ein ziemlich kleines Gebiet (Radius etwa 1000 m),
—die Verteilung erfolgt ungleichmässig.
Die Versuchsergebnisse waren zufreidenstellend, so dass weitere Versuche mit verbesserten Mitteln geplant sind.

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L'UTILISATION de radioisotopes pour le marquage d'insectes, en vue d'étudier certains aspects de leur comportement, est connue depuis déjà quelques années,[1] et cette technique est actuellement en plein développement surtout aux U.S.A.[2-4] Le présent rapport décrit une expérience de ce type réalisée en France avec le concours de l'Institut National de Recherches Agronomiques, promoteur de l'expérience, et du Commissariat à l'Energie Atomique.

L'expérience réalisée fut le marquage d'une ruche d'abeilles pour contrôler et étudier leur secteur de butinage. Nous étudierons ici, plus spécialement, les problèmes soulevés par le choix et la manipulation des éléments radioactifs, les résultats d'ordre biologique étant développés plus particulièrement dans une revue spécialisée.[5]

CHOIX DE L'ÉLÉMENT RADIOACTIF

L'isotope choisi doit, autant que possible, présenter les caractéristiques suivantes:

(1) *Avoir une période de quelques jours seulement*, afin d'éviter toute contamination prolongée aussi bien de la ruche que des ressources mellifères prospectées par la colonie.

(2) *Etre émetteur γ de moyenne énergie*, afin de le rendre assez facilement détectable tout en minimisant les doses susceptibles d'être reçues.

(3) *N'être pas nocif aux abeilles*. Elles sont, par exemple, sensibles au ClNa à des teneurs supérieures à 1 g/l.

(4) *S'intégrer facilement à la nourriture* de la colonie sans y précipiter, ni floculer.

(5) *Avoir une période biologique suffisante.*

Les conditions restrictives précédentes nous ont conduits à choisir comme élément l'or-198 de période 2,7 jours, émettant entre autres, un gamma de 0,411 MeV. Bien que l'on puisse envisager l'utilisation d'autres radioisotopes, le fait que l'or radioactif puisse être livré sous forme d'une solution colloïdale facilement assimilable et manipulable, a fortement influencé notre choix.

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ACTIVITÉ DE LA SOLUTION

Le calcul de l'activité à introduire par individu a été fait en supposant qu'une abeille en vol passant à environ 30 cm d'un détecteur à scintillation en double le bruit de fond, supposé de 50 c/s. Ceci conduit à choisir une activité d'environ 1 μc par abeille, soit une activité globale de 40 mc pour une colonie de 40.000 individus, en supposant l'activité uniformément répartie entre chaque abeille. Un calcul approximatif de la dose reçue dans ces conditions par abeille, durant une période biologique supposée de trois jours, donne un total de 600 roentgens. Cette dose peut paraître importante, mais DAVIS et NAGEL[6] ont employé des activités allant jusqu'à 20 μc par insecte, et WHITING[7] a montré qu'aucun effet n'était décelable pour des irradiations d'insectes allant jusqu'à 54.000 roentgens.

Cette activité fut donc administrée au moyen de glucose, nourriture habituelle des abeilles, dans lequel on incorpora le produit radioactif. La solution de glucose doit être tamponnée avec de l'acide tartrique, pour ramener le pH de la solution à 5,5, assurant ainsi la stabilité du colloïde.

RÉALISATION EXPÉRIMENTALE

Une préétude en laboratoire (marquage d'une ruchette de 1.000 abeilles) ayant fourni des résultats satisfaisants, nous avons effectivement réalisé le marquage d'une colonie d'environ 40.000 individus.

La composition chimique de la solution

radioactive utilisée est la suivante:

Or	3,5 mg/cm³
Gélatine	30 mg/cm³
Glucose	1 mg/cm³
NaCl	5 mg/cm³

Taille moyenne des particules. environ 300 Å.

Cette solution, d'un volume initial de 5 cm³, fut diluée dans 1,5 litre de glucose.

La manipulation eut lieu sur le toit même de la ruche. Le glucose est situé dans un nourrisseur placé lui-même au centre du toit. La solution radioactive était contenue dans un flacon de 15 cm³ et protégée par un container de plomb de 4 cm d'épaisseur. Le liquide est extrait au moyen d'une seringue et d'une aiguille hypodermique. La Fig. 1 explicite clairement la manipulation.

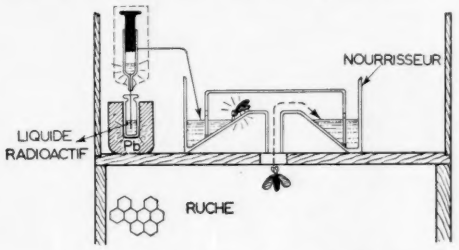

FIG. 1. Principe de la manipulation.

RÉSULTATS

Dans l'expérience précédemment décrite, les abeilles n'absorbèrent au cours d'une nuit que la moitié de la nourriture qu'elles ont l'habitude de prendre pendant le même temps. Nous constations donc une certaine répugnance des abeilles pour la solution ajoutée, fait que nous avions déjà remarqué dans notre expérience en laboratoire. Nous vîmes ainsi la dose prévue de 1 microcurie par abeille diminuer de moitié; mais par contre, le glucose restant dans le nourrisseur fut absorbé dans les jours qui suivirent, donnant une certaine stabilisation du marquage des abeilles.

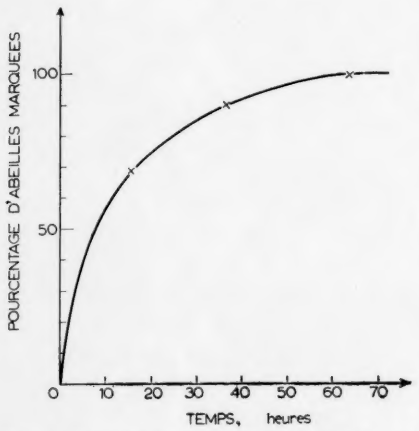

FIG. 2. Répartition de l'activité dans la colonie.

La courbe de la Fig. 2 montre que le marquage est total au bout de trois jours.

D'autre part, les ruches immédiatement voisines contenaient environ 1 pour cent d'abeilles marquées, les ruches plus éloignées n'en contenaient pas. Ceci confirme le fait déjà connu, de la non communauté de deux ruches voisines (appelée également phénomène de dérive).

Quant à la quantité de produit radioactif effectivement prise par chaque abeille, aucune statistique n'a été établie sur ce point, mais nous pouvons quand même affirmer qu'elle est très variable.

La deuxième partie de la manipulation consistait à détecter les abeilles marquées dans leur secteur de butinage. Pour cela, nous avons utilisé un détecteur portatif à scintillation* équipé d'un cristal INa (Tl) de diamètre $1\frac{1}{4}$ pouce et de hauteur $1\frac{1}{2}$ pouce. Nous attrapions les abeilles à l'aide d'un filet à papillons à mailles fines, et approchions ensuite à loisir l'abeille du détecteur. Ce procédé a l'avantage de faciliter la prise des abeilles posées dans des endroits inaccessibles à la sonde (branche haute d'un arbre par exemple).

1.009 abeilles furent mesurées et 17 marquées furent retrouvées; les plus lointaines étaient éloignées d'environ 1,5 km de la ruche à vol d'oiseau, et la distance

* De marque "Victoreen", le Scintillac modèle 641.

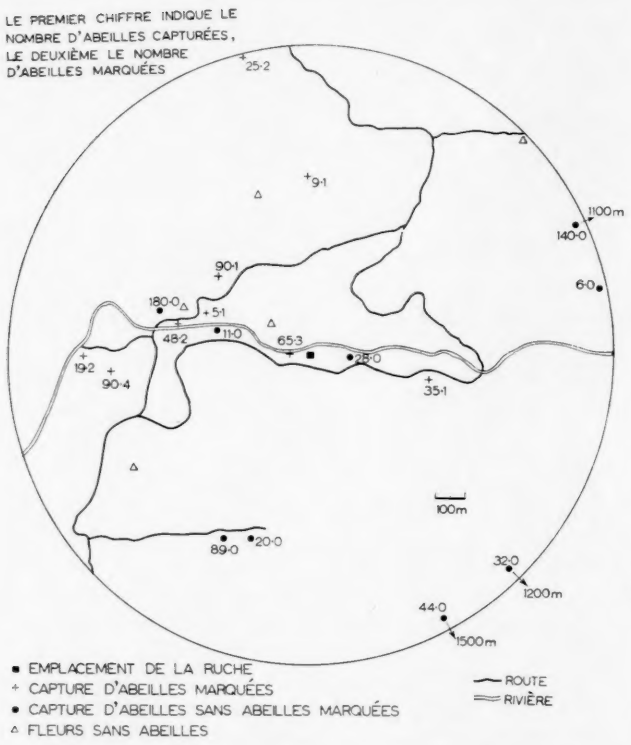

FIG. 3. Plan de la zone prospectée.

moyenne était de 600 à 700 m. Certes, le nombre d'abeilles retrouvées est relativement faible, mais compte tenu des faits suivants, il représente quand même une valeur assez sûre de la réalité:

— Sur l'ensemble du terrain prospecté se trouvaient plusieurs ruchers représentant environ 30 colonies.

— Des champs où, par exemple, nous trouvions 3 abeilles marquées sur 30 ou 40, étaient rapidement abandonnés, puisque nous avions acquis la certitude que les abeilles de notre ruche les prospectaient. Par contre, dans les champs où nous ne retrouvions aucune abeille marquée, nous continuions à collecter jusqu'à 100 à 200 abeilles pour acquérir plus de certitude sur la non prospection de ces terrains. Nous joignons, pour plus de clarté, un schéma de la topologie des lieux, sur lequel les zônes étudiées sont indiquées, ainsi que les endroits où furent retrouvées des abeilles marquées (Fig. 3).

Nous conclurons en disant que cette expérience s'est avérée suffisamment fructueuse pour que nous envisagions de la renouveler avec des moyens de détection accrus. C'est seulement ainsi que nous pourrons recueillir suffisamment de renseignements isolés pour pouvoir en extraire des conclusions qui soient peu influencées par les erreurs dûes aux phénomènes statistiques.

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The Synthesis of Non-random Copolymers by the Gamma Irradiation of Emulsion Systems

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(*Received* 28 *January* 1959)

γ-Irradiation of vinyl monomers emulsified in polymer latices has been shown to be a useful method for the synthesis of non-random copolymers. Examples include the copolymerization of methyl methacrylate and butyl methacrylate with both styrene and vinyl acetate. The reactions are complete after a relatively small dose and no provision need be made to exclude air.

The reaction products were separated by fractional precipitation techniques.

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LA SYNTHÈSE DES COPOLYMÈRES NON AU HASARD PAR L'IRRADIATION GAMMA DES SYSTÈMES D'ÉMULSIONS

L'irradiation γ des monomères viniques émulsifiés dans des réseaux polymériques s'est montrée une méthode utile pour la synthèse des copolymères non au hasard. Les exemples comprennent la copolymérisation du methacrylate methylique et du methacrylate butylique avec la styrène ainsi qu'avec l'acétate vinique. Les réactions s'accomplissent après une dose rélativement petite et sans le besoin d'exclure l'air.

Les produits de la réaction furent séparés par les méthodes de la précipitation fractionnaire.

СИНТЕЗ СОПОЛИМЕРОВ С УПОРЯДОЧЕННОЙ СТРУКТУРОЙ ПУТЕМ ГАММА-ОБЛУЧЕНИЯ ЭМУЛЬСИОННЫХ СИСТЕМ

Показано, что облучение виниловых мономеров, эмульгированных в полимере, является надежным методом синтеза сополимеров с упорядоченной структурой. Приводятся примеры сополимеризации метилметакрилата и бутилметакрилата со стиролом и с винилацетатом. Реакции заканчиваются после облучения сравнительно небольшой дозой и при этом не требуется принимать меры для удаления воздуха. Разделение продуктов реакции производилось посредством фракционированного осаждения.

DIE SYNTHESE VON NICHT-STATISTISCH VERTEILTEN COPOLYMEREN DURCH γ-BESTRAHLUNG VON EMULSIONSSYSTEMEN

Die γ-Bestrahlung von Vinylpolymeren, emulgiert in Polymergittern, ist eine brauchbare Methode zur Synthese von nicht-statistisch verteilten Copolymeren. Die Copolymerisation von Methylmethacrylat und Butylmethacrylat zusammen mit Styrol und Vinylacetat wurde durchgeführt. Die Reaktionen sind vollzogen nach Bestrahlung mit relativ kleinen Dosen und es muss dabei nicht unter Luftabschluss gearbeitet werden.

Die Reaktionsprodukte wurden durch fraktionierte Fällung getrennt.

INTRODUCTION

Copolymers in which the monomer units are not distributed at random along the chain may be synthesized by polymerizing vinyl monomers in the presence of polymers. Such reactions fall into two categories. First those in which the polymer contains groups or positions which can be decomposed, usually by heat, thus initiating polymerization of the monomer and secondly, those in which the copolymerization is initiated by transfer from the growing polymer chain.

Examples of reactions in the first category include those which involve the synthesis of special polymers containing reactive groups. These may be thermally or chemically activated to yield free radicals which subsequently initiate the polymerization of the added monomer. For instance, heat labile perester groups can be introduced into poly (methyl acrylate) to serve as sites for the grafting of styrene.[1] Use of phthalyl peroxide to initiate the polymerization of styrene enables residual peroxide groups to be incorporated into the polymer. Subsequent heating of this polymer decomposes the peroxide groupings, thereby initiating the polymerization of added methyl methacrylate to form block copolymers.[2]

Various types of radiation have been used to produce free radical sites on polymer molecules. For instance, the photolysis of poly (methyl vinyl ketone) in the presence of acrylonitrile by ultra-violet light has been used to obtain graft polymers.[3]

Similarly, ultra-violet light will break the C–Br bond in a specially synthesized polystyrene containing bromine end groups. On photolysing such polymers in methyl methacrylate solution, copolymerization takes place.[4]

γ-Radiation has proved useful for the preparation of non-random copolymers. Ballantine *et al.*[5] have irradiated polymer substrates either mixed or in contact with the copolymerizing monomer. Excessive homopolymerization is minimized by ensuring contact between the polymer and monomer. Despite efficient initial mixing, its maintenance during polymerization is dependent upon solvation and diffusion of the monomer into the polymer. By this technique acrylonitrile has been grafted to polythene, and to poly (dimethyl siloxane) in the form of silicone rubber. Styrene has been grafted to poly (methyl methacrylate), polyethylene and polytetrafluoroethylene.[6]

Rubber has been similarly copolymerized with methyl methacrylate[7] by irradiation of a rubber–monomer mixture. A similar copolymerization can also be achieved by using rubber latex mixed with the monomer.[8,9]

In the second category i.e. those in which the chain transfer mechanisms are postulated, graft copolymers have been prepared by polymerizing vinyl acetate, in the presence of poly (methyl methacrylate), using benzoyl peroxide as the catalyst.[10] Hayes,[11] using a persulphate catalyst in an emulsion system has synthesized copolymers of vinyl acetate with both poly (vinyl chloride) and polyacrylonitrile.

Polymerization in emulsion systems has the advantage that high conversions may be obtained without the increase in reaction medium viscosity encountered in the corresponding bulk reaction and this eliminates mixing difficulties. Furthermore high reaction rates can be obtained using a Co^{60} source of γ-radiation.

This paper describes a method of initiating the non-random copolymerization of a number of vinyl monomers with various preformed vinyl polymers using γ-radiation.

EXPERIMENTAL MATERIALS AND METHODS

Material

Commercially supplied monomers were freed from inhibitors by shaking with 10% aqueous sodium hydroxide followed by thorough washing with water. The monomers were dried with anhydrous calcium chloride. The emulsions were stabilized by "Manoxal O.T.", used as a 3·75% wt/vol aqueous solution.

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Irradiation

Emulsions were irradiated by γ-radiation from a 700 c Co^{60} source previously described.[12]

Methods

The polymer latices were generally made by the radiation initiated polymerization of an emulsion containing four parts of monomer in sixteen parts of the 3·75% wt/vol soap solution. The emulsions, contained in stoppered test-tubes, immersed in a water bath at 17 $\pm$ 1°C, were irradiated at a dose rate of $8{\cdot}8 \times 10^4$ rep/hr. Provided that the emulsions had been thoroughly shaken for an hour or so, the observed rates of polymerization could be reproduced.

Conversions to polymer were measured, either by recording the volume contraction which occurred on polymerization, or by determination of the solid content of the latex. The volume contractions were measured dilatometrically by observations through an optical system. Two methods were used in determining the polymer content of the latex. The first was to weigh the polymer isolated by coagulation of the latex in a precipitant; the second, to weigh the residue remaining after the latex had been dried at 120°C correcting for the soap content. The results from all these methods were in good agreement with one another.

Having prepared the latex and ensured maximum conversion of the monomer, the copolymerizing monomer was added, usually in the ratio of two volumes of monomer to ten of latex. After shaking for an hour or so, to ensure thorough emulsification of the monomer, the latex was irradiated under conditions similar to those described above until polymerization was complete. The reaction product obtained contains some homopolymer formed by the polymerization of the added monomer, some unchanged polymer and finally copolymer.

Isolation of the product was carried out by a number of methods depending upon the components of the polymer system. In some cases the latices were dissolved in acetone and then precipitated in methanol. In others they were coagulated directly by pouring into methanol or aqueous salt solution. Removal of the last traces of soap can be ensured only by further reprecipitations.

Fractional precipitation

The components of the isolated product were separated by fractional precipitations, which involve the slow addition of a precipitant to a vigorously stirred solution of the product. After precipitation of the least soluble component, the precipitate is separated and then more non-solvent is added and the cycle repeated.

The fractional precipitations were performed on 1% solutions of the polymer. The actual solvent–precipitant combination adopted depended on the component polymers. The precipitant was added dropwise at a rate of 0·2 ml per min to 10 or 20 ml of the polymer solution, contained in a centrifuge tube and stirred continuously. As was expected, the product separated into three distinct fractions: unchanged polymer, copolymer and polymer resulting from the homopolymerization of the added monomer. The onset of precipitation was observed by the appearance of a faint turbidity which, on centrifuging at 2500 rev/min for 20–30 min, was sedimented leaving a clear supernatant liquid. The first fraction was always the most difficult to sediment, owing to its small particle size. The supernatant liquor was decanted off and to it was added further precipitant. More polymer precipitation was immediately evident. A turbidity invariably remained after centrifuging until sufficient precipitant had been added for all the second (i.e. copolymer) fraction to flocculate. Addition of non-solvent over the range between the precipitation of the first and second fractions produced little or no further sediment, even after centrifuging it for several hours, despite the continued existence of a turbidity. The flocculation of the copolymer occurred at the addition of only a single drop of non-solvent, a change in the stirred solution being easily identifiable. At this point, centrifuging easily sedimented the flocculated polymer and the supernatant

liquid was quite clear. This sudden precipitation probably indicates the coiling of that component of the copolymer corresponding to the homopolymer yet to be precipitated and the copolymer sol particles are then unstable and consequently flocculate. After a further addition of non-solvent, precipitation of the last fraction took place. Between the flocculation of the copolymer sol and the appearance of this second turbidity, there was invariably a range over which further addition of non-solvent produced no sign of precipitation. Centrifuging easily sedimented the turbidity and the supernatant liquid was clear. Continued addition of non-solvent completed the precipitation.

Of the three fractions thus obtained, infra-red analysis showed that 95 per cent of the first fraction was pure homopolymer, the second, i.e. copolymer fraction, contained some of each reacting species, whilst the last fraction was pure homopolymer of the other reaction component.

One possible explanation of the presence of a small percentage of the second component in the first fraction is that some of the copolymer or other homopolymer has co-precipitated with the first homopolymer. Similarly, coprecipitation and cosolvation could be responsible for some quantity of each of the homopolymers being precipitated with the copolymer. A second possibility is that on pouring off the supernatant liquid after centrifuging, a trace of the solution remains with the sedimented precipitate.

To examine these possibilities, solutions containing known quantities of the two pure homopolymers prepared by similar methods and known quantities of previously fractionated copolymers were fractionally precipitated. The results showed good recovery efficiencies for each component. Furthermore, infra-red analysis confirmed the largely unchanged composition of each fraction except in the case of the first fraction which contained amounts ranging up to 5 per cent of the other polymeric component. Repeated attempts at further fractionation of the copolymer precipitates failed to split them.

Such tests on each of the fractionation techniques used here demonstrated their essential efficiencies, particularly in the case of the second and third precipitates.

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RESULTS

The emulsion polymerization of vinyl acetate by γ-radiation

During the preliminary investigations, it was considered desirable to accumulate some information on the emulsion polymerization by γ-radiation of each monomer used. As an example, some observations on the polymerization of vinyl acetate are mentioned.

The polymerization was followed dilatometrically, the observed volume contraction being converted into the percentage of reaction using the values of 0·925 and 1·187 for the densities of monomer and polymer respectively at 17°C. Fig. 1 shows the course of a typical polymerization of vinyl acetate monomer emulsified in an equal volume of the standard soap solution. This irradiation was carried out at 17°C in a field intensity of $8{\cdot}8 \times 10^4$ rep/hr, the emulsion being contained in a stoppered dilatometer from which no precaution had been taken to remove air. An inhibition period was always observed, but its extent varied as the surface area of the emulsion exposed to the air was

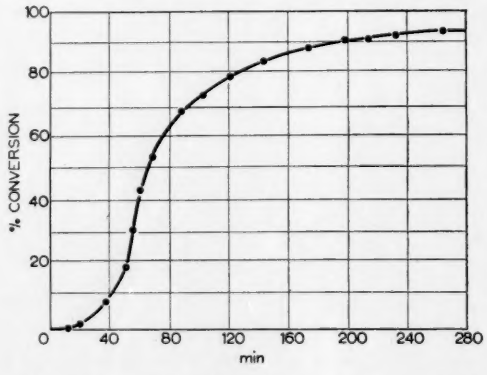

FIG. 1. The γ-irradiation initiated emulsion polymerization of vinyl acetate.

changed. Flushing the emulsion with oxygen-free nitrogen, prior to and during irradiation, decreased the inhibition period. The irradiation of an emulsion, prepared and maintained under high vacuum conditions, showed almost no inhibition. In each case, the rates of polymerization after the induction period were approximately equal.

The copolymerization of vinyl monomers with addition polymers

1. Poly (butyl methacrylate)–vinyl acetate. Latices of poly (butyl methacrylate), were made by irradiation of an emulsion containing four parts of monomer in sixteen parts of the 3·75% wt/vol soap solution, at 17°C. Samples never received doses of more than $3{\cdot}5 \times 10^5$ reps and in each case were analysed to ensure that polymerization was complete.

To these 20 per cent PBM latices was added monomeric vinyl acetate in quantities to give weight ratios of PBM to VA varying from 1 to 8. After shaking for more than 1 hr, the latices were irradiated at $8{\cdot}8 \times 10^4$ rep/hr. Polymerizations were complete in less than 4 hr.

Product isolation was effected by coagulating the latex in boiling dilute aqueous salt solution. The fractionations were carried out on either this coagulated polymer or on polymer which had been reprecipitated in water from a solution in acetone.

Fractional precipitations were performed from 1% wt/vol acetone solutions, using water or a 50 : 50 methanol–water mixture. The use of water containing a trace of either calcium chloride or sodium chloride seemed to aid the precipitation of the poly (vinyl acetate) fractions.

In each fractionation technique adopted, preliminary experiments were performed to show its effectiveness in separating a mixture of the two relevant homopolymers. These homopolymers were prepared by methods typical of those used in the copolymerization reactions. As an example, the results of a separation of a 50 : 50 mixture of poly (butyl methacrylate) and poly (vinyl acetate) are shown in Fig. 2. At all stages of the addition of precipitant the centrifuged solutions were clear, never turbid.

Figs. 3 and 4 show the results of fractional precipitation using water and 1 : 1 methanol–water mixtures respectively on products resulting from the irradiation of poly (butyl methacrylate) latices mixed with vinyl acetate. Evaporation and losses during the transference of solutions from the centrifuge tubes cause apparent deviations in the volumes of non-solvent required for the precipitation of the second and third fractions.

2. Polyvinyl acetate–butyl methacrylate. These copolymers were synthesized by the irradiation, at 17°C, of latices containing 20 per cent polyvinyl acetate into which had been imbibed sufficient butyl methacrylate to give a 1 : 1 weight ratio of polymer to monomer. Isolation and fractionation procedures were identical to those described for the PBM–VA systems. Comparing Figs. 4 and 5, it is obvious that a lower proportion of product is in the form of a copolymer than in the PBM–VA system. In this case, infra-red analysis showed the copolymer contained one part by weight of butyl methacrylate to three of vinyl acetate.

3. Poly (butyl methacrylate–styrene). This copolymerization was effected by γ-irradiation, at 17°C, of a latex which originally contained 20 per cent PBM and into which had been emulsified styrene, equal in weight to the polymeric substrate present. Product isolation was by coagulation in salt water or methanol.

Fig. 6. illustrates a fractional precipitation performed by the addition of methanol to a 1% benzene solution of the polymer. From a mixture of the homopolymers, polystyrene precipitated sharply at 18 per cent methanol, whilst PBM precipitated later on at 58 per cent. However, from the copolymerization reaction mixture, the precipitation of the polystyrene takes place over a range of methanol addition. Such retarded precipitation is probably due to limited cosolvation of the polystyrene fraction by the copolymer, but the bulk of any added polystyrene has been shown to be recovered well before

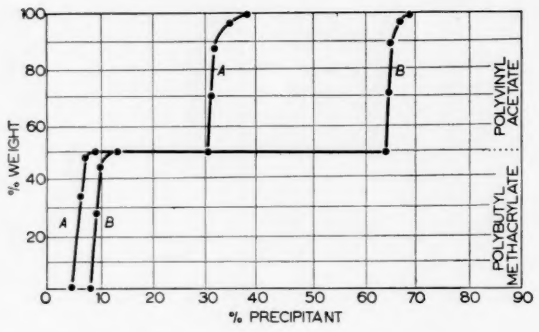

FIG. 2. Fractional precipitation of 1 : 1 mixtures of PBM and PVA from acetone solution. (A) using water as precipitant and (B) using water/methanol as precipitant.

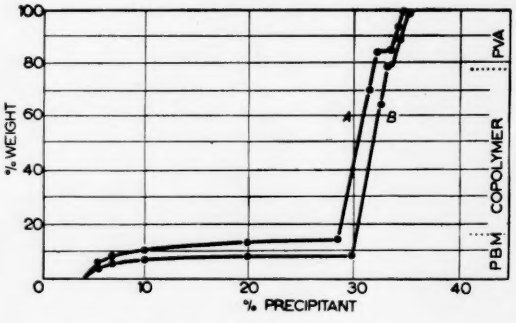

FIG. 3. Fractional precipitation of reaction products of PBM and VA from acetone solution using water as precipitant. (A) PBM : VA = 2 : 1. (B) PBM : VA = 1 : 1.

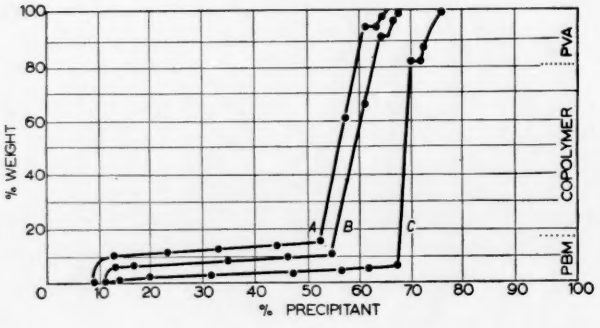

FIG. 4. Fractional precipitation of reaction products of PBM and VA from acetone solution using water/methanol as precipitant (A) PBM : VA = 6 : 1. (B) PBM : VA = 4·5 : 1. (C) PBM : VA = 1 : 1.

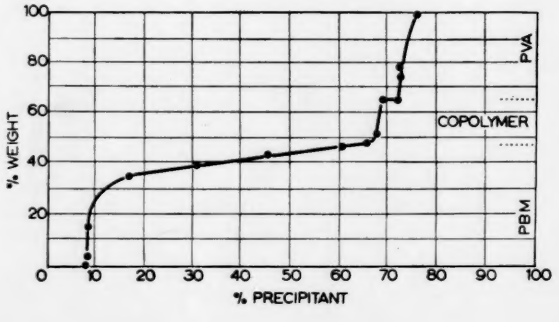

FIG. 5. Fractional precipitation of reaction products of PVA and BM (1 : 1) from acetone solution using water/methanol as precipitant.

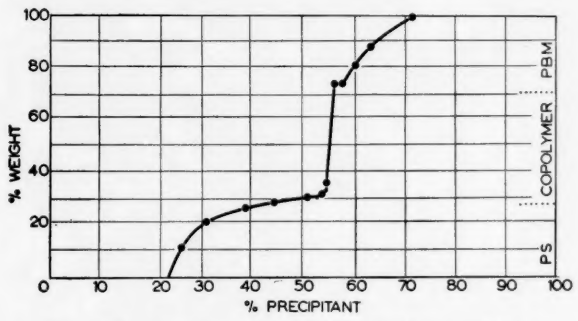

FIG. 6. Fractional precipitation of reaction products of PBM and styrene from benzene solution using methanol as precipitant. (PBM : styrene 1 : 1.)

flocculation of the copolymer begins. Infrared analysis showed the first fraction to be 95 per cent polystyrene, and that the copolymer fraction contained 42 per cent polystyrene and 58 per cent butyl methacrylate. The last fraction was pure poly (butyl methacrylate).

4. Poly (methyl methacrylate)–styrene. Emulsions containing equal volumes of methyl methacrylate, aqueous soap solution and water were irradiated at $8{\cdot}8 \times 10^4$ rep/hr at 17°C for not more than 4 hr in stoppered test-tubes or dilatometers. When polymerization was complete, monomeric styrene was emulsified into the latex by thoroughly shaking the mixture for a few hours. The resulting latex was re-irradiated at the same dose rate as before until polymerization of the styrene was complete. This normally required about 4 hr irradiation.

The latex was coagulated by pouring it into either aqueous salt solution or methanol. Further purification necessitated reprecipitation in petroleum ether or methanol from a benzene solution.

For this copolymerization reaction, the products were fractionally precipitated from benzene solutions in two ways. The first used methanol as the non-solvent and the second, petroleum ether (b.p. 100–120°C). Using methanol, the polystyrene was precipitated first; petroleum ether, on the other hand, precipitated the poly (methyl methacrylate) first.

Figs. 7 and 8 show the results of such fractionations using methanol and petroleum ether respectively as the non-solvent.

The usual tests for solution and precipitation complications showed that the utilization of methanol as precipitant effected a good separation of the components. However using petroleum ether as the non-solvent permits only a separation of the styrene homopolymer fraction from the reaction product, since extensive coprecipitation occurs between the methyl methacrylate homopolymer and the copolymer fractions. Prior removal of the methyl methacrylate homopolymer from the reaction product by the methanol fractional precipitation technique does allow a good separation of the copolymer and the styrene homopolymer to be achieved in a subsequent fractionation using petroleum ether. Such a result is shown in Fig. 8, curve B. Furthermore, a methanol fractional precipitation on the poly (methyl methacrylate)–copolymer coprecipitate, obtained in a petroleum ether precipitation, does effect a clean separation of the two components.

The amount and compositions of each of the three components in the reaction product, as separated using these various fractional precipitation procedures, showed a good agreement.

By varying the composition of the reaction feed, copolymers of differing composition may be prepared. For example, the copolymer obtained using a 1 : 1 mixture contained 40 per cent methyl methacrylate;

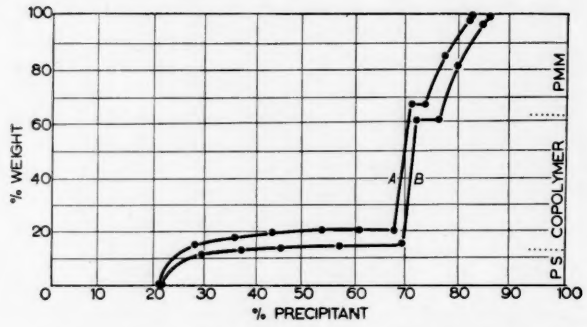

FIG. 7. Fractional precipitation of reaction products of PMM and styrene from benzene solution using methanol as precipitant. (A) PMM : styrene 1 : 1. (B) PMM : styrene 3·3 : 2.

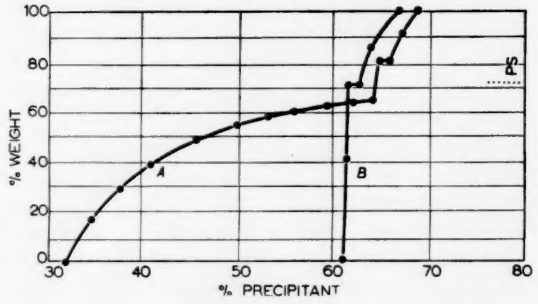

FIG. 8. Fractional precipitation of reaction products of PMM and styrene from benzene solution using petroleum ether (100–120°C) as precipitant. (A) PMM : styrene 1 : 1 and (B) the same after the methyl methacrylate homopolymer has been removed by fractional precipitation with methanol.

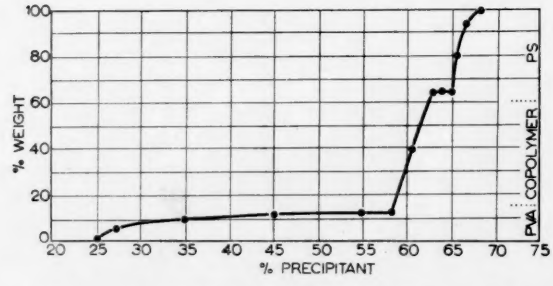

FIG. 9. Fractional precipitation of reaction products of PVA and styrene 1 : 1 from benzene solution using petroleum ether (b.p. 100–120°C) as precipitant.

whilst that obtained from the 3·3 : 2 polymer–monomer mixture contained 50 per cent methyl methacrylate.

5. Poly (vinyl acetate)–styrene. Copolymerization of styrene to polyvinyl acetate was attempted using the standard recipe and method. Product isolation was by coagulation of the latex in salt solution, followed by reprecipitation from a benzene solution into petroleum ether.

Results of a fractional precipitation, using benzene as solvent and petroleum ether (b.p. 100–120°C) as precipitant, are shown in Fig. 9. Infra-red analysis on the copolymer showed that its composition was 63 per cent vinyl acetate and 37 per cent styrene.

6. Poly (methyl methacrylate)–vinyl acetate. Poly (methyl methacrylate) latices, containing 33 per cent polymer, were made as previously described and to them was added monomeric vinyl acetate in amounts such that its weight equalled that of the polymer. After irradiation in the usual manner, the polymer was recovered by dissolving the latex in acetone and precipitating the solution in water, or by directly coagulating the latex in salt solution. Fractional precipitations were effected from 1% acetone solutions using a 1 : 1 methanol–water mixture as the non-solvent. The results are shown in Fig. 10, curve A.

7. Poly (vinyl acetate)–methyl methacrylate. Methyl methacrylate was emulsified in latices containing 20 per cent PVA. Irradiation, isolation and fractionation procedures were similar to those used in the preparation of PMM–VA copolymers. Fig. 10, curve B, shows the result of a fractional precipitation on the product resulting from reacting a 1 : 1 ratio of monomer and polymer.

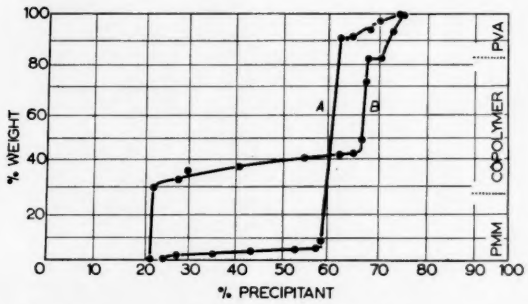

FIG. 10. Fractional precipitation of reaction products of (A) PMM : VA = 3·3 : 2 and (B) PVA : MM 1 : 1 from acetone solution using water/methanol as precipitant.

DISCUSSION

The precise mechanism of these copolymerization reactions has yet to be elucidated, but a tentative scheme is proposed and discussed in the light of preliminary results.

Homopolymerization may be initiated by radicals originating from the radiolysis of water diffusing into the latex particles and reacting with the monomer (1). Radicals are also formed by the direct action of γ-radiation on the monomer itself (2). Further sites of homopolymerization result from transfer of propagating chains with the monomer (6 and 7).

Copolymerization can be initiated by free radical centres formed on the polymer. These may originate from several reactions; firstly by the direct action of high energy radiation on the polymer (3), secondly by hydroxyl radical attack (4), and thirdly by transfer with propagating chains (5). Propagation could occur from each of these radical centres by reaction with monomer.

Two general categories of termination are feasible. The first, reaction between growing chains and radicals from water (8), and the second, bimolecular macroradical reactions.

Reaction (10) would produce homopolymers whilst reaction (9) forms homopolymer only if disproportionation were operative.

Homopolymer of each variety may also be formed by random scissions of the chains by the incident radiation.

$$R_w\cdot + M \rightarrow R_wM\cdot \quad (1)$$

$$M \rightarrow M\cdot \xrightarrow{nM} M_n\cdot \quad (2)$$

$$P \rightarrow R\cdot \xrightarrow{nM} RM_n\cdot \quad (3)$$

$$P + R_w\cdot \rightarrow R\cdot + R_wH \quad (4)$$

$$M_n\cdot + P \rightarrow R\cdot + M_n \quad (5)$$

$$RM_n\cdot + M \rightarrow RM_n + M\cdot \quad (6)$$

$$M_n\cdot + M \rightarrow M_n + M\cdot \quad (7)$$

$$RM_n\cdot + R_w\cdot \rightarrow \text{Termination} \quad (8)$$

$$M_n\cdot + R_w\cdot \rightarrow \text{Termination} \quad (9)$$

$$M_n\cdot + M_n\cdot \rightarrow \text{Termination} \quad (10)$$

$$RM_n\cdot + M_n\cdot \rightarrow \text{Termination} \quad (11)$$

$$RM_n\cdot + RM_n\cdot \rightarrow \text{Termination} \quad (12)$$

Polymer → Degradation and cross-linking.

$R_w\cdot$ = radicals from radiolysis of water

M = monomer

P = polymer substrate

$MM_n\cdot$ = propagating homopolymer radical

$RM_n\cdot$ = propagating copolymer radical.

The presence of oxygen will undoubtedly affect some of these reactions, notably the initiation and propagation steps, by its addition to the various radicals involved. This manifests itself primarily in the observed inhibition period but secondary effects may include the subsequent decomposition of the product of these oxidation reactions. The oxygen may also affect the radiation induced degradation of the polymers present.

The relative importance of the copolymerization reaction compared with the homopolymerization of the added monomer will be governed by their relative rates of initiation. Those systems including polymers which are particularly susceptible to the effect of ionizing radiation might be expected to be effective copolymerization systems. The possibility of radical formation on the polymer, by abstraction reaction with radicals formed in the radiolysis of the water diffusing into the latex particles, must also be considered. Furthermore, the reactivity of any radicals formed on the polymer may also influence the proportion of copolymerization.

The results are summarized in Table 1, the first column of which lists the reacting species and the second column shows the composition of the product. The figures quoted are for reactions between equal masses of reactants except for the polyvinyl acetate–styrene copolymerizations, in which the ratio is 3·3 to 2.

TABLE 1

Reactants		Product composition		
A	*B*	Poly-*A*	Copolymer	Poly-*B*
BM	VA	8·1	71·8	20·1
VA	BM	48·7	17·1	34·2
BM	St	25·2	42·3	32·5
MM	St	32·2	46·8	21·0
VA	St	12·1	52·4	35·5
MM	VA	5·2	85·2	9·6
VA	MM	18·3	38·3	43·4

The yield of copolymer is appreciable in each of the systems studied. It is apparent that the methacrylate polymers serve as very efficient copolymerization substrates: polyvinyl acetate is less efficient. Preliminary results indicate that polystyrene is inefficient as a copolymerization substrate for butyl methacrylate. The sequence of these efficiencies parallels the accepted order of susceptibilities of the polymers towards ionizing radiation.

Polyvinyl acetate seems to act more efficiently as a substrate with styrene than with the methacrylate monomers. This is the inverse of that expected from the relative reactivities of the monomers with polyvinyl acetate radicals. However the polyvinyl acetate radicals involved in the present non-random copolymerization are probably not those involved in random copolymerizations.

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It is possible that the homopolymerization of styrene is comparatively slower than that of the methacrylate monomers, and hence copolymerization is favoured with styrene.

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Activation Analysis for Selenium in Ore Concentrates, Slags and Waste Gases Obtained in a Metallurgical Industry

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The purpose of this investigation was to check, by means of activation analysis, a chemical method used at the Boliden Mining Company in Sweden for the determination of selenium. Various ways of performing the activation analysis of selenium on the materials in question were investigated. It was found that when the ratio of selenium γ-activity to γ-activity of higher energy was higher than about 0·01, a spectrometric activation analysis could be done. In other cases a chemical activation analysis method could be used. The use of a special spectrometric activation analysis method by means of the γ-cascades of selenium was also investigated.

Three samples were analysed by chemical activation analysis. The results were in good agreement with those obtained using the chemical method employed by the company (deviation less than 15 per cent).

The possibility of using activation analysis for the selenium in waste gases was also investigated. Spectrometric activation analyses of gas samples contained in quartz ampoules were performed. No radiation due to selenium could be detected. Thus only an upper limit (50 μg/l.) for the selenium content could be established.

L'ANALYSE PAR ACTIVATION DU SÉLÉNIUM DANS LES CONCENTRÉS DE MINERAIS, LES SCORIES ET LES GAZ PERDUS PRODUITS PAR UNE INDUSTRIE MÉTALLURGIQUE

Le but de cette recherche était de vérifier, par l'analyse par activation, une méthode chimique pour le dosage du sélénium employée chez la Compagnie Minière Boliden en Suède. La recherche se fit sur des moyens différents d'achever l'analyse par activation du sélénium dans les matières en considération. On trouva que lorsque la proportion de l'activité γ du sélénium à l'activité γ d'énergie plus forte était supérieure à environ 0,01, une analyse par activation spectrométrique pouvait s'employer. Dans des autres cas une méthode chimique d'analyse par activation pouvait être employée. On examina aussi une méthode spéciale d'analyse par activation spectrométrique au moyen des cascades γ du sélénium.

Le dosage de trois échantillons par l'analyse par activation chimique fut accompli. Les résultats étaient en bon accord avec ceux donnés par la méthode chimique dont se sert la compagnie (variation moins de 15 pour cent).

On rechercha aussi la possibilité d'employer l'analyse par activation pour le sélénium dans les gaz perdus. Les analyses par activation spectrométriques d'échantillons de gaz contenus dans des ampoules de quartz furent accomplies; on ne pouvait découvrir aucune radiation dûe au sélénium. Ainsi put-on établir seulement une limite supérieure (50 μg/l.) pour le contenu de sélénium.

ОПРЕДЕЛЕНИЕ СЕЛЕНА В РУДНЫХ КОНЦЕНТРАТАХ, ШЛАКЕ И ОТРАБОТАННЫХ ГАЗАХ ПРИ ПОМОЩИ АКТИВАЦИОННОГО АНАЛИЗА

Настоящее исследование имеет целью проверку, при помощи активационного анализа, химического метода определения селена, который применяется Горнорудным Обществом Болиден в Швеции. Были использованы различные способы определения селена в соответствующих материалах. Найдено, что спектрометрический активационный анализ возможен, когда отношение гамма-активности селена к гамма-активности с более высокой энергией превышает ~0,01. В других случаях более пригодным оказался химический активационный анализ. Была исследована также возможность применения специального спектрометрического активационного анализа с помощью каскадного γ-излучения селена.

Три образца были исследованы методом химического активационного анализа. Данные этого анализа показали хорошее совпадение с результатами, полученными химическим методом, применявшимся Обществом (расхождение было меньше 15%).

Ъыла рассмотрена также возможность определения селена в отработанных газах методом активационного анализа. Спектрометрическому активационному анализу были подвергнуты образцы газа, содержащиеся в кварцевых ампулах. Излучения от селена обнаружено не было. Таким образом, удалось установить только верхний предел содержания селена (50 μг/л).

AKTIVIERUNGSANALYSE DES SELENS AN ERZKONZENTRATEN, SCHLACKEN UND ABGASEN DER METALLINDUSTRIE

Der Zweck dieser Untersuchung war die Überprüfung der chemischen Methode der schwedischen Boliden Mining Gesellschaft zur Bestimmung von Selen mit Hilfe der Aktivierungsanalyse. Verschiedene Verfahren zur Durchführung der Aktivierungsanalyse des Selens in den in Frage kommenden Materialien wurden untersucht. Es zeigte sich, dass eine spektrometrische Aktivierungsanalyse dann durchführbar ist, wenn das Verhältnis der Selen-γ-Aktivität zur höher energetischen γ-Aktivität grösser ist als 0,01. Ausserdem wurde eine spezielle spektrometrische Aktivierungsanalysen-Methode unter Verwendung der γ-Kaskaden des Selens versucht.

3 Proben wurden durch chemische Aktivierungsanalyse untersucht. Die Ergebnisse zeigten gute Übereinstimmung mit den durch chemische Analyse erhaltenen Ergebnissen der obengenannten Gesellschaft (die Abweichung betrug weniger als 15 Prozent). Die Möglichkeit, mit Hilfe der Aktivierungsanalyse Selen in den Abgasen zu bestimmen, wurde untersucht. Dabei wurde die spektrometrische Aktivierungsanalyse in Gasproben, die in Quarzampullen eingeschlossen waren, durchgeführt. Es konnte keine dem Selen zuordenbare Strahlung aufgefunden werden. Daher konnte für den Selengehalt nur eine obere Grenze von 50 μg/l. angegeben werden.

RADIOACTIVATION ANALYSIS

The principles of activation analysis have been reviewed in several papers[1,2] and will not be discussed here. There are two main types of activation analysis:

(1) chemical activation analysis where the element to be determined is separated chemically to radiochemical purity before radioactivity measurements are performed, and

(2) spectrometric activation analysis where the element is determined in the material without chemical treatment by analysing the γ-spectrum of the material.[3]

The instrumentation involved in the latter has been described by several scientists.[4,5,6,7,8] In γ-ray spectra the area under the peak due to γ-rays from a certain

element is proportional to the amount of the radioactive isotope giving that particular γ-radiation. By comparing this area for the element to be determined in the sample under test with that resulting from a standard of the same element—both substances having been irradiated at the same time and place—it is possible to obtain the required analysis data.

The sensitivity of the activation analysis is different for different elements.[9,10] It depends on the amount of radioactivity resulting from the element after a certain time of irradiation and thus depends on the neutron cross-section of the element and the half-life of the isotope formed. The lowest quantitatively detectable amount of selenium is calculated to be about 0·1 μg at a flux of 10^{12} n/sec per cm^2 and with 30 days irradiation when using spectrometric activation analysis and 0·01 μg when using chemical activation analysis. Activation analysis is thus a very sensitive method for analysing selenium. It has been used by PUTMAN *et al.* to determine the selenium content of decolorized glass.[11]

Nuclear data of selenium

The neutron irradiation of selenium produces two radioactive isotopes of useful half-lives, Se^{75} with a half-life of 121 days and Se^{81m} with a half-life of 57 min. Selenium-75 is formed from Se^{74} which comprises 0·87 per cent of natural selenium, while Se^{81m} is formed from Se^{80} which comprises 49·8 per cent of natural selenium. Selenium-75 decays by means of electron capture and γ-radiation of various energies while Se^{81m} decays to Se^{81} by isomeric transition and γ-radiation and further by β-radiation (Fig. 1).[12]

The formation neutron cross-section for Se^{75} is 26 barns and for Se^{81m} 30 mbarns.[13] In spite of the great difference in the percentage abundances of the two isotopes in natural selenium, the amounts of radioactivity from the two isotopes after twelve days irradiation are about the same because of the great difference in the neutron cross-sections. Hence, the use of Se^{81m} for activation analysis does not result in a higher sensitivity but does result in a gain of time—Se^{81m} building up to half of the saturation

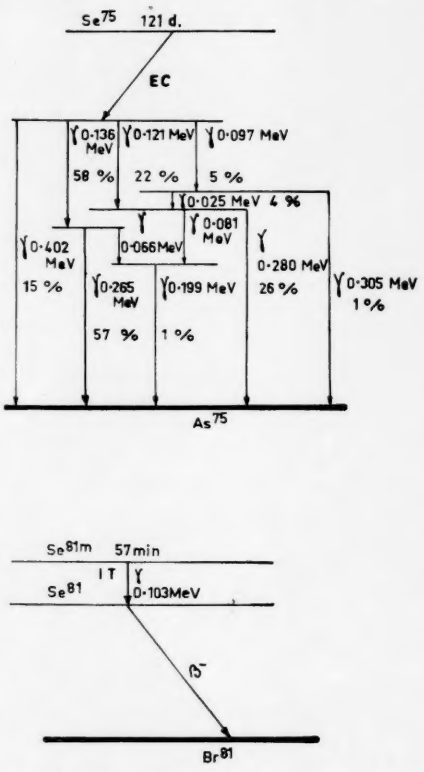

FIG. 1. Decay-schemes for Se^{75} and Se^{81m}.

activity after about 1 hr of irradiation. The irradiation time necessary to give the same amount of Se^{75} radioactivity is 6 days.

Possible methods for activation analysis of selenium

The different ways for performing this determination of selenium are:

(1) a spectrometric activation analysis,
(2) a chemical activation analysis and
(3) for Se^{75}, a more complicated spectrometric activation analysis in which the two pairs of γ-quanta, emitted in cascade (Fig. 1), are used.[14]

The factor that determines which way is the most suitable one is the γ-background which depends on the composition of the material to be analysed. In the spectrometric method both Se^{75} and Se^{81m} can be used. However, Se^{75} is preferable for the actual samples as a disturbing γ-background

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can be reduced by ageing. For the chemical activation analysis of the materials to be analysed only Se^{75} can be used as the chemical method is time-consuming (about 1 day). Thus Se^{75} was the selenium isotope chosen for the whole work.

Three materials from different stages of the production of copper were investigated. Material 1 was a slag, material 2 an arsenic concentrate and material 3 a copper concentrate. Each material was studied separately to find the best method—it turned out, however, to be the same one for all three materials.

ACTIVATION ANALYSIS OF SLAGS AND ORE CONCENTRATES

Irradiation and preparation of samples and standards

The material was placed in a polythene bottle and irradiated, together with the selenium standard, for 14 days at a flux of $4 \cdot 10^{11}$ n/sec per cm^2. Initially, selenium powder, enclosed in a PVC bag, was used as a standard. It was found, however, that the bag became soft during irradiation and took up part of the selenium powder, thus making the recovery of selenium rather difficult. This was overcome by using a selenium standard in the form of a pellet (10–20 mg). After irradiation, the pellet was taken out of the PVC bag, in which it had been irradiated, and reweighed. It was thereafter dissolved in conc. HNO_3 and made up to a certain volume. A suitable known amount of this solution was then used as an actual standard for the experiments.

Spectrometric activation analysis

For the spectrometric activation analysis, a scintillation detector with a cylindrical 1 in. diameter × 1 in. thick thallium activated NaI crystal was connected to a single channel analyser through a linear amplifier. The width of the channel was set at 2 per cent of the energy range (2 V of 100 V range) and the channel moved at a constant speed over the spectrum. The pulses from the analyser were fed to a rate meter and then to a recorder which thus registered the γ-spectrum. The γ-peaks from Se^{75} most suitable for measurement are the unresolved pair of peaks at 121 and 136 keV respectively. The 121 keV peak is emitted in 22 per cent of all disintegrations and the 136 keV in 58 per cent. Thus the latter peak is dominating. Fig. 2 shows a γ-spectrum of irradiated selenium obtained after ageing until Se^{81m} had disappeared. As the γ-energies of Se^{75} are rather low, radioactive isotopes of elements with γ-radiation of higher energies will interfere with the photopeaks of Se^{75} by giving a high γ-background, due to Compton distribution and back-scattered radiation. In the materials analysed, there were several elements (iron, cobalt, antimony, zinc) which were expected to cause serious trouble.

Spectra of the three materials investigated were recorded one day after the irradiation. No γ-peak due to selenium could be detected.

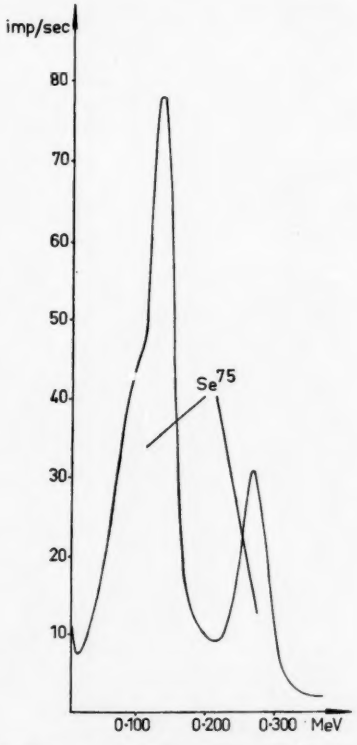

FIG. 2. Gamma spectrum of irradiated selenium after ageing until Se^{81m} has decayed (1 in. diameter × 1 in. thick thallium activated NaI crystal).

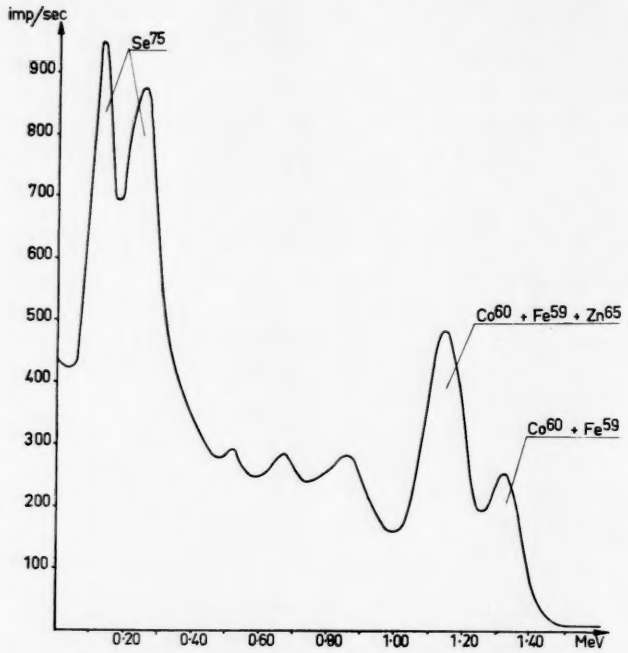

FIG. 3. Gamma spectrum of irradiated copper concentrate after ageing for three weeks (1 in. diameter × 1 in. thick thallium activated NaI crystal).

After ageing for three weeks, a γ-energy peak at 136 keV could be detected in the spectrum from materials 2 and 3 but not in the spectrum from material 1. The calculated selenium activity after this period of time as well as the γ-activity of higher energy due to other elements is shown in Table 1.

TABLE 1. Calculated selenium activity and γ-activity of higher energy

Material	Selenium activity (μc/g)	Other activities (μc/g)
1	0·03	100
2	0·9	100
3	0·5	40

As seen from the table, material 1 shows a much higher total γ-activity, in comparison with the selenium activity, than the other materials. Fig. 3 shows a γ-spectrum of material 3. This is the most favourable material from the point of view of the selenium analysis. Two selenium peaks can be seen but it is impossible to determine directly the total area of either of them. A subtraction method was, however, devised for determining the area of the 136–121 keV peak. Antimony, iron and cobalt, the most disturbing elements, were irradiated and the γ-spectra of suitable amounts of each element were recorded in the same geometry as the samples were measured. These spectra were subtracted, after normalization of the intensities of the photo-peaks, from the γ-spectrum of the material. In this way, the 136–121 keV selenium peak became more defined but the uncertainty in its area was still about $\pm$20 per cent. The uncertainty when using this method for material 2 was even greater.

Spectrometric activation analysis using coincidence techniques

A spectrometric analysis was also tried using the two pairs of γ-cascades of selenium,

namely 136 keV followed by 265 keV (58 and 57 per cent respectively of the total number of disintegrations) and 121 keV followed by 280 keV (22 and 26 per cent abundance respectively). The samples were viewed by two equal scintillation detectors which were, via pulse height analysers adjusted at the γ-cascade energies of selenium, coupled in coincidence in such a way that pulses were registered only when γ-quanta of around 130 keV and 270 keV fell into the detectors simultaneously. Because the energies of the two γ-cascades are so similar (121 and 280 respectively 136 and 265 keV), both cascades could be employed at the same time as one single pair of cascades. This means that 80 per cent of the photo-absorbed γ-quanta of selenium can be used. However, the apparatus also registers accidental coincidences, the number of such coincidences being linearly related to the resolution time of the coincidence circuit. For materials 2 and 3, the accidental coincidences drowned the selenium cascades at the coincidence resolving time of 10^{-6} sec. It was found that the resolving time must be of the order of 10^{-8} sec, to make an analysis for selenium possible in these materials by the method. For material 1, the situation was still more unfavourable. No other equipment was available to us at the time of the analysis but work has been commenced on a three-channel fast–slow coincidence system,[15] which will offer a smaller resolving time with preserved energy selection.

Chemical activation analysis

In this method, the samples were treated by means of the following procedure which has been described by the Association of Official Agricultural Chemists[15] and modified by Olofsson at the Boliden Mining Company.

Chemical treatment of samples. Dissolution of the sample: 0·1–1 g of the irradiated material was weighed and transferred to a crucible of iron or nickel. A weighed amount of selenium (10–100 mg) was mixed thoroughly with the sample and then 25 g Na_2O_2 was mixed in. The mixture was covered with a thin layer of Na_2O_2 and thereafter melted by means of an electrical furnace which produced a temperature of 900°–1000°C. The crucible was moved round carefully during the heating. As soon as the melt flowed easily, the heating was stopped. When the crucible had cooled down, it was placed in a 400 ml beaker containing 50 ml H_2O. After the melt had dissolved, the crucible was taken out and washed. The solution was cooled and neutralized with H_2SO_4 (1 : 1). Hereafter, 50 ml conc. H_2SO_4 was added under rapid stirring and the resultant liquid evaporated on a water bath to a volume of 100 ml.

Separation of SiO_2: When the material contained much SiO_2 (materials 1 and 2), this substance was separated in the following way. The solution was first boiled for 15 min. After cooling to 60–70°C, 15 ml 5% gelatin solution was added in drops while stirring. Air was bubbled through the solution for 30 min. Hot water (50 ml) was added to the solution which was then filtered. The filtrate was evaporated to a volume of about 100 ml.

Distillation of selenium: The cool solution was placed in a distillation flask. 100 ml HBr (48%), to which 7 ml Br_2 had been added, was poured in and the mixture was then distilled into a beaker containing 10 ml H_2O; 40–50 ml distillate was collected.

Precipitation of selenium: The distillate was neutralized with NH_4OH until the Br_2 colour had disappeared. 10 ml HCl and 1–2 g hydrazine sulphate were added. After having settled for 12 hr, the precipitate was filtered off and washed with water and ethanol. Care was taken that no selenium was left sticking to the walls of the filter crucible. The precipitate was dried at 105°C and weighed. The precipitates, obtained from materials 2 and 3 which contained rather a lot of arsenic, were dissolved in Br_2–HBr solution and the selenium was precipitated again.

Chemical treatment of the standard solution. A known amount of the carrier selenium solution was added to a certain amount of the standard selenium solution. The mixture was evaporated to dryness on a water bath, 15 ml HCl (HCl : H_2O = 74 : 3) was added and the solution heated until the nitrous gases had disappeared. The resultant liquid was diluted and 1–2 g hydrazine sulphate added. The precipitate was filtered as above.

In the experiments reported below the irradiated material and its standard were aged for two weeks and then treated as described above. The activities of the selenium precipitates were measured with a scintillation detector (1 in. diameter × 1 in. thick thallium activated NaI crystal), connected to a scaler and the amount of selenium in the various materials was

calculated. Corrections for losses of selenium occurring during the procedure were made. The radiochemical purity of the precipitates was tested by γ-spectrometry.

In the preliminary experiment on material 3 (cf. Table 2) the standard consisted of irradiated selenium powder which had been removed from the plastic by dissolving the latter in acetone and filtering.

TABLE 2. Preliminary data for the selenium analysis of material 3

Amount of material (g)	0·889
Carrier (mg Se)	14·84
Recovered amount of Se (mg)	11·13
Counts/min of Se from material 3	40000
Amount of Se standard (mg)	2·40
Counts/min of Se standard	292000
% Se in material	0·051

Tables 3 and 4 contain the most reliable data obtained for the various materials and standards (Se pellets). The maximum error in the selenium content obtained by the chemical activation analysis method was estimated to be ± 5 per cent.

TABLE 3. Data for irradiated standards

	Material		
	1	2	3
Amount of Se standard (mg)	0·0447	0·1025	0·1138
Carrier (mg Se)	27·00	27·00	27·00
Recovered amount of Se (mg)	15·55	18·96	19·05
(counts/min)	450·2	5423	4931
(counts/min corrected for losses)	781·5	7760	7015
Counts/min per μg Se standard	68·1	75·7	61·7

Discussion of results

It is evident from the experiments that simple spectrometric activation analysis with the apparatus described cannot be used to determine the selenium in material 1 and would only give values of low accuracy for materials 2 and 3. Generally, it can be said that there are great difficulties involved in determining selenium by simple spectrometric activation analysis when the ratio of

TABLE 4. Data for irradiated materials

	Material		
	1	2	3
Amount of material (g)	0·8608	0·1836	0·1269
Carrier (mg Se)	87·94	30·04	31·00
Recovered amount of Se (mg)	69·17	16·74	22·77
Counts/min of Se from material	1567	5418	3263
Counts/min per μg Se standard	68·1	75·7	61·7
μg Se in dissolved sample	29·2	129	72·3
% Se in material	0·0034	0·070	0·056

selenium γ-activity to γ-activity of higher energy is lower than about 0·01. When this is the case, it is thought possible to determine selenium spectrometrically by means of γ-ray coincidence spectrometry.

A chemical activation analysis of materials containing 0·001–0·1 per cent of selenium can easily be performed if the material is soluble. The lower limit for the determination of selenium in this way at an irradiation time of 30 days and a flux of $4 \cdot 10^{11}$ n/sec per cm^2 was calculated to be about 0·1 μg if the measurements were performed with a scintillation detector of the type described with a geometrical efficiency of about 10 per cent.

Since a chemical activation analysis of good accuracy could be performed on all the materials studied, this method was chosen as the best procedure for analysing, by activation, the materials for selenium. Since the selenium losses in the chemical procedure were obtained by means of the selenium carrier, there can be very little chance of any further errors caused by uncorrected losses. The only possibility would be a difference in

TABLE 5. Selenium data obtained by different analysis methods

Material	% Se (Chem. act. anal.)	% Se (Chem. anal.)
1	0·0034	0·003
2	0·070	0·08
3	0·051*	0·048
	0·056	

* Value obtained at preliminary analysis.

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chemical behaviour between the irradiated selenium and the carrier selenium due to differing chemical states, e.g. during the dissolution procedure, if not all of the irradiated selenium were dissolved, or during the distillation. As far as we have been able to control the process, no such losses occurred. Table 5 shows the data obtained compared with the mean values of results obtained colorimetrically,[16] and titrimetrically.[17]

ANALYSIS OF SELENIUM IN WASTE GASES

Activation analysis of selenium in waste gases from one stage of the production of copper has also been performed.

Spectrometric activation analysis was the only possible activation analysis method for analysing the gases since no reliable way of absorbing selenium and performing a chemical activation analysis could be devised. The irradiation was performed in quartz ampoules. Quartz gives rise to several short-lived activities due partly to impurities in the material but only very few long-lived activities can be detected. This makes the work with Se^{75} very favourable since a long ageing period (10–100 days) gives an almost inactive quartz ampoule while most of the Se^{75} activity is still left.

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Procedure

80 cm^3 of gas was enclosed in a quartz ampoule which had been washed carefully with bichromate cleaning mixture and water. It was then irradiated for 14 days together with an ampoule filled with ordinary air. Gamma-spectra of the two ampoules were taken after one and four months ageing.

Results

No difference in the γ-spectra of the two ampoules could be detected. Thus only an upper limit of the selenium content in the waste gas could be calculated, 50 μg Se/l. gas. This gave a lower value for the limit than simple activity measurements, the explanation of this probably being that the gases contained other materials, apart from selenium, giving rise to long-lived activities.

Note added in proof:

After the completion of this paper a very extensive report on activation analysis has been given in:
LEDDICOTTE G. W. *et al.*, The use of activation analysis in analytical chemistry. Second U.N. Int. Conf. on the Peaceful Uses of Atomic Energy. P/927.

The authors report activation analysis sensitivity figures for a large number of elements. For selenium, both radiochemical and spectrometric methods have been developed and the observed minimum concentrations are 0·001 p.p.m. Se in animal tissue (radiochemically) and 0·01 p.p.m. Se in ceramics (spectrometrically).

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Mr. D. GILLAM has revised the English manuscript.

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Photoradiochromatography—Method for the Study of Chromatograms with Radioactive Substances

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It is shown that a photographic film is sensitive enough to record the light emitted during the operation of halogen filled Geiger–Müller counters.

This fact is applied in studying distributions of radioactivity in chromatograms to obtain the equivalent of autoradiographs with very much improved sensitivity.

The method can be made quantitative by the use of a calibration chart relating optical density to number of discharges in the Geiger–Müller counter.

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LA PHOTORADIOCHROMATOGRAPHIE—UNE MÉTHODE POUR L'ÉTUDE DES CHROMATOGRAMMES À L'AIDE DES CORPS RADIOACTIFS

On démontre qu'une pellicule photographique est assez sensible pour enregistrer la lumière émise pendant le fonctionnement d'un compteur Geiger–Müller rempli d'halogène.

Ce fait s'applique à l'étude de la distribution de la radioactivité dans les chromatogrammes pour obtenir l'équivalent des autoradiographes avec une sensibilité beaucoup augmentée.

La méthode peut être rendue quantitative par l'emploi d'une graphique d'étalonnage qui rapporte la densité optique au nombre de décharges dans le compteur Geiger.

ФОТОРАДИОХРОМАТОГРАФИЧЕСКИЙ МЕТОД ИССЛЕДОВАНИЯ ХРОМАТОГРАММ ПРИ ПОМОЩИ РАДИОАКТИВНЫХ ВЕЩЕСТВ

Показано, что фотопленка достаточно чувствительна, чтобы регистрировать световое излучение, испускаемое при работе счетчика Гейгера–Мюллера, наполненного галоидом.

Этот факт используется при исследовании распределения радиоактивности и позволяет получать хроматограммы, не уступающие по чувствительности лучшим радиоавтограммам.

Применение градуировочной таблицы зависимости оптической плотности от числа разрядов счетчика Гейгера–Мюллера позволяет сделать метод количественным.

PHOTORADIOCHROMATOGRAPHIE—EINE METHODE ZUR UNTERSUCHUNG VON CHROMATOGRAMMEN MIT HILFE RADIOAKTIVER SUBSTANZEN

Es wird gezeigt, dass ein photographischer Film empfindlich genug ist, um das Licht, das von einem Halogen-gefüllten Geiger-Müller-Zähler ausgesandt wird, zu registrieren.

Bei der Untersuchung radioaktiver Zonen in Chromatogrammen erzielt man mit beschriebenen Methode gewissermassen Autoradiogramme, wobei der Geiger-Müller-Zähler als Verstärker der Sensibilität des Filmes dient.

Weiterhin wird eine quantitative Auswertbarkeit der Methode durch Beziehung der optischen Dichte auf die Anzahl der Entladungen im G-M-Zähler aufgezeigt.

INTRODUCTION

It is well known that, associated with the discharge in a Geiger counter, there is photoemission, corresponding to the de-excitation of metastable atoms of the noble filling gas. It follows that in the sensitive volume of the counter, during the discharge, there are points where ultraviolet and visible light is emitted.

This light emission, associated with the discharge in spark counters and Geiger–Müller counters is easily detected with a photomultiplier, as shown by Baptista and Ramalho[1] and by Yamasaki and Okano.[2] Charpak and Renard[3] have studied the light emission from a proportional counter in the same way.

As the light intensity is fairly high, it was suggested by one of us[4] that the photographic film is a simple and convenient means of detecting it.

It is to be expected that the light emission associated with a discharge will be related to the charge per pulse, since the number of metastable atoms as well as the number of positive ions increases with the applied potential. The intensity is also expected to be higher for equivalent pulse amplitudes in halogen than in vapour-quenched counters, because of the de-excitation which persists in the body of the counter after the discharge.[5]

EXPERIMENTAL STUDY

During this work a Geiger–Müller counter with a mica window 2 mg/cm^2 thick and a gas filling of neon, argon and bromine (Philips 18514) was used. The photographic film was the Ilford Medical Standard X-ray film.

The variation of the light output with the potential applied to the detector was studied by placing the tube over the photographic film. For each value of the applied potential, a different part of the film was exposed to 2000 discharges, and the pulse amplitude v was observed. After development, the optical densities D corresponding to the different applied potentials V were measured. The variation of v and D with V are shown in Fig. 1, together with a part of the counter plateau. It is evident that both the optical density and the pulse amplitude vary linearly with the applied potential over a wide range.

It was established also that the optical density decreased from the centre to the walls of the detector, as expected from the distribution of light sources in the counter.

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THE PHOTORADIOCHROMATOGRAM

The high sensitivity of the photographic method and its simplicity by comparison with counting methods makes it particularly suitable for scanning radioactive chromatograms of low activity.

The photographic recording of light corresponding to limited radioactive zones in the chromatogram can be regarded as a form of autoradiography in which the G.M. counter acts as an amplifier to enhance the sensitivity of the photographic film.

Fig. 2 shows the experimental arrangement. The film and chromatogram were mounted side by side and traversed across a collimating slit 5 mm wide under the end-window counter. The clearance between the counter and the film was about 3 cm in order to obtain more uniform optical density. The scanning speed was 1·3 cm/min.

Fig. 3 is a calibration chart showing optical density of the film as a function of the counting rate in these conditions.

With the help of this calibration chart the method can be made quantitative. From the optical densities of the photoradiochromatogram with the help of the calibration chart of Fig. 3 the counting rate corresponding to the radioactive zones was calculated. In Fig. 4 we see that an identical distribution is obtained with the photoradiochromatogram

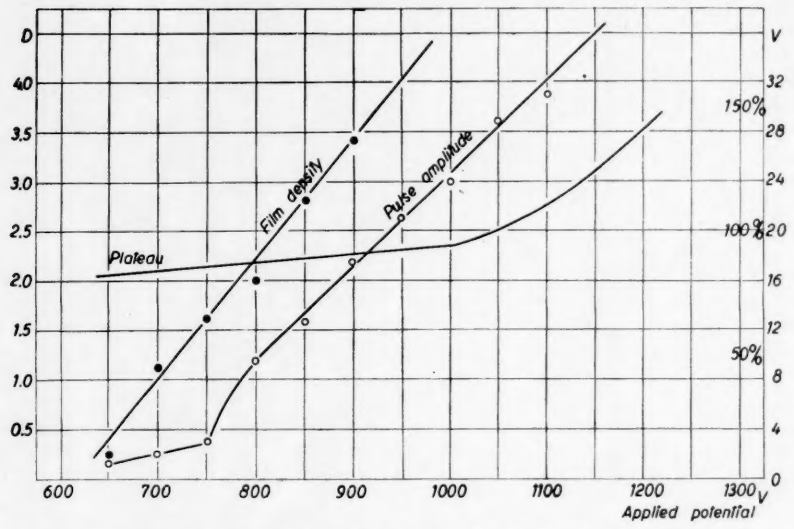

FIG. 1. Optical density D of the film, amplitude of the G.M. pulses v (volts) and G.M. plateau as function of the operating potential.

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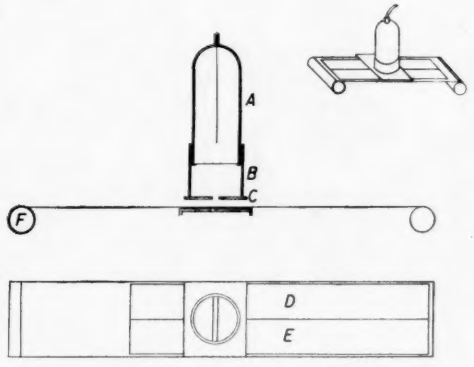

FIG. 2. Arrangement for photoradiochromatography:
A—G.M. counter *B*—collimator
C—diaphragm *D*—chromatogram
E—film *F*—motor

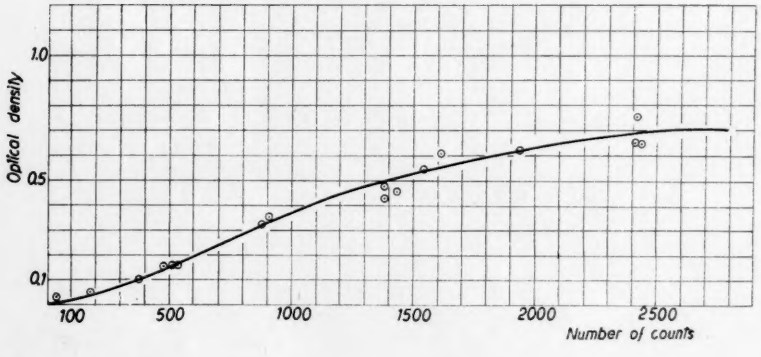

FIG. 3. Calibration chart for Ilford Medical Standard X-ray film with halogen quenched G.M. detector: optical density versus number of pulses.

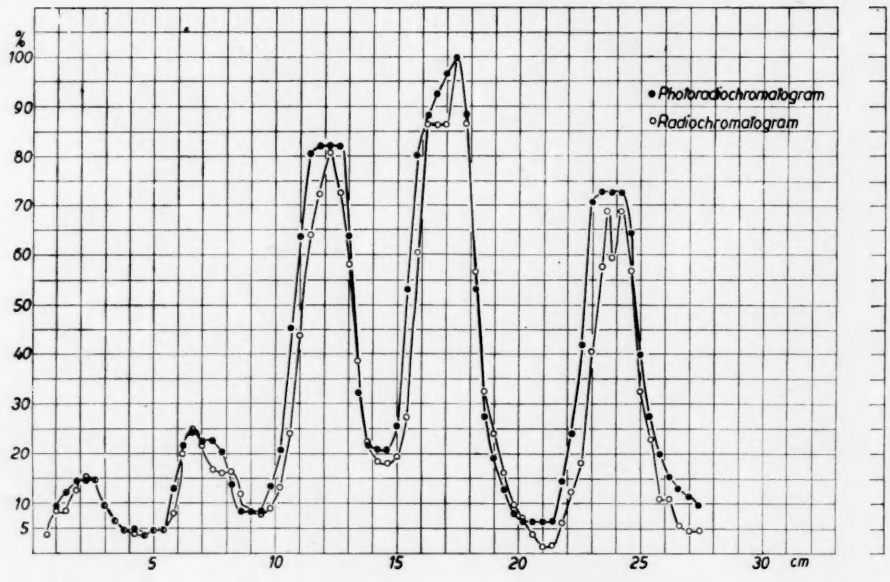

FIG. 4. Radioactive distributions (normalized) obtained from a photoradiochromatogram and the corresponding radiochromatogram.

and with a radiochromatogram obtained in the usual way with the same scanning speed. The curves are normalized for the point of maximum radioactivity.

The usefulness of the method as a substitute for the direct autoradiography of chromatograms is evident from Fig. 5, which shows side by side an autoradiograph obtained by 7 days exposure and a photoradiochromatogram obtained in 30 min from the same chromatogram with identical film. The method can be particularly useful when the activity of a chromatogram is too low for direct autoradiography, especially if the half-life of the radioactive tracer is short.

SENSITIVITY CONTROL

The presence of a strong ultraviolet component in the light emitted by the counter was shown by interposing a 1 mm thick glass plate between its window and the film. It is likely that the photographic sensitivity can be enhanced by using ultraviolet sensitive film or by sensitizing standard film with a wave-length shifter, such as paraffin oil.

However, for most purposes it is sufficient to increase the light output by adjusting the potential applied to the detector (see Fig. 1). In this way, counting rates very little above background can be registered easily.

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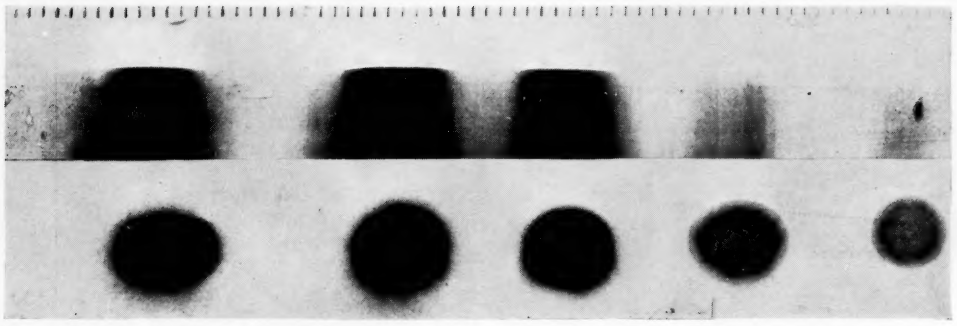

FIG. 5. Above: an autoradiography of a chromatogram (exposure time 7 days); below: the corresponding photo-radiochromatogram (30 min).

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Improved Plastic Well Scintillators for Beta Counting

Determination of Exchangeable Potassium in Man Using Low Doses of Isotope

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In making measurements of exchangeable potassium in man, the dose usually employed is 250–350 μc of K^{42}. When mixing time is extended to 40 hr after injection of the tracer, accurate assay is difficult, even when using this dose. However, the advent of the plastic scintillator has made possible the construction of very sensitive well counters for β-detection. A new counter of this type is described, which counts K^{42} at 15 per cent efficiency in liquid samples of 90 ml volume. Using this counter, measurements of exchangeable potassium can be made by using the specific activity of urine samples obtained 40 or more hr after administration of only 50 μc of K^{42}. Such urine samples usually have counting rates ranging from 1000 to 2000 counts per min above a background of 150 counts per min. Data are given showing the mixing of 50 μc of K^{42} in a healthy man up to 60 hr after tracer administration. The values for exchangeable potassium in this man were computed on the basis of each of four urine samples voided later than 40 hr after injection. These four values for exchangeable potassium had a mean of 4181 m. equiv., with standard deviation 63 m. equiv.

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DES SCINTILLATEURS PLASTIQUES À PUITS DE FORME SUPÉRIEURE POUR LE COMPTAGE DES BÉTAS: MESURE DU POTASSIUM ÉCHANGEABLE CHEZ L'HOMME, UTILISANT DE PETITES DOSES D'ISOTOPE

Pour les mesures du potassium échangeable chez l'homme, la dose employée est ordinairement 250–350 μc de K^{42}. Quand on étend la période de mélange jusqu'à 40 hr après l'injection de l'indicateur, il est difficile de faire une mesure précise, même en employant une telle dose. Cependant l'invention du scintillateur plastique a rendu possible la mise en point des compteurs à puits très sensibles pour les rayons β. On décrit un nouveau compteur de ce genre, qui compte le K^{42} avec une efficacité de 15 pour cent dans des échantillons liquides de 90 ml de volume. Avec ce compteur on peut mesurer le potassium échangeable au moyen de l'activité spécifique d'échantillons d'urine obtenus 40 hr ou plus après l'administration de seulement 50 μc de K^{42}. De tels échantillons d'urine ont d'habitude des taux de comptage dans la rangée 1000 à 2000 comptes par minute audessus d'un fond de 150 comptes par minute. On fournit des données qui démontrent le mélange de 50 μc de K^{42} chez un homme sain jusqu'à 60 hr après l'administration de l'indicateur. Les valeurs de potassium échangeable chez cet homme furent calculées pour chacun de quatre échantillons d'urine évacués plus de 40 hr après injection. La moyenne de ces quatre valeurs pour le potassium échangeable était 4181 m. équivalents, la variation normale étant 63 m. équiv.

УСОВЕРШЕНСТВОВАННЫЕ ПЛАСТИЧЕСКИЕ СЦИНТИЛЛЯЦИОННЫЕ БЕТА-СЧЕТЧИКИ С КАНАЛОМ ДЛЯ ПОМЕЩЕНИЯ ОБРАЗЦОВ. ОПРЕДЕЛЕНИЕ ОБМЕННОГО КАЛИЯ У ЧЕЛОВЕКА ПРИ ПОМОЩИ МАЛЫХ ДОЗ ИЗОТОПА

При определении обменного калия у человека вводимая доза обычно составляет 250–350 μк K^{42}. Если время, прошедшее после введения изотопа, превышает 40 часов,

то точное определение, даже при такой дозировке, становится затруднительным. Однако применение пластических сцинтилляторов дало возможность сконструировать очень чувствительные счетчики β-частиц. Дано описание нового счетчика этого типа, который измеряет K^{42} с точностью до 15% в объеме жидкости в 90 мл. Этот счетчик позволяет измерять обменный калий по удельной активности образцов мочи, взятых через 40 и больше часов после введения всего только 50 μк K^{42}. Удельная активность таких образцов обычно находится в пределах от 1000 до 2000 имп/мин над фоном, составляющим 150 имп/мин. Приводятся данные по проникновению 50 μк K^{42} у здорового человека за промежуток времени до 60 часов после введения изотопа. Значения обменного калия для данного индивидуума были получены для каждого из четырех образцов мочи, выделенных позже, чем через 40 часов после инъекции. Среднее из этих четырех значений обменного калия составляет 4181 м.экв., со стандартным отклонением в 63 м.экв.

VERBESSERTE PLASTIK-BOHRLOCHSCINTILLATOREN FÜR β-MESSUNG

Die üblicherweise verwendete Dosis bei Messungen des Kaliums im Menschen beträgt 250–350 μc K^{42}. Dauert die Vermischungszeit länger als 40 Stunden nach Injektion des Indikators, wird auch bei Verwendung einer so grossen Dosis eine genaue Messung schwierig. Seit jedoch Plastik-Scintillatoren zur Verfügung stehen, besteht die Möglichkeit, für die β-Messung sehr empfindliche Bohrlochzähler herzustellen. Ein neuer derartiger Zähler wird hier beschrieben, welcher K^{42} mit 15 prozentiger Ausbeute in Flüssigkeitsproben von 90 cm^3 zu messen gestattet. Mit Hilfe dieses Zählers kann die Messung des austauschbaren Kaliums mittels der spezifischen Aktivität von Harnproben 40 oder mehr Stunden nach Anwendung von nur 50 μc K^{42} ausgeführt werden. Solche Harnproben haben für gewöhnlich 1000–2000 Teilchen pro Minute über einem Hintergrund von 150 Teilchen/Minute. Die angeführten Daten zeigen den Vermischungsgrad von 50 μc K^{42} in einem gesunden Mann 60 Stunden nach Injektion des Indikators. Die Werte für das austauschbare Kalium wurden in diesem Fall berechnet aus jeweils einer von 4 Harnproben, welche mehr als 40 Stunden nach der Injektion gesammelt wurden. Diese 4 Werte für das austauschbare Kalium ergeben im Mittel 4181 m. äquiv. mit einer Standardabweichung von 63 m. äquiv.

In making measurements of exchangeable potassium in man, it has been customary to employ doses of K^{42} ranging from 250 to 350 μc.[1,2] These doses of isotope permit measurement of K^{42} activity in urine or serum samples taken 24 hr after administration of the tracer to adult human beings, using Geiger–Müller tubes as detectors. It has been reported recently by O'Meara *et al.*[3] that mixing of K^{42} in man is significantly prolonged in those patients who have edema. It was concluded by these authors that in order to ensure optimum accuracy, equilibrium periods of 40 hr should be used when measuring exchangeable potassium in sick patients.

When a mixing time of 40 hr is used, K^{42} passes through more than three half-lives between administration and sampling, so that only 11 per cent of the administered dose remains. Most of the data available have been taken using a mixing period of 24 hr, at which time 26 per cent of the administered K^{42} remains. If 350 μc of K^{42} are given to adult human beings, one can, by concentrating the specimen, still measure the activity in urine samples voided 40 hr after dose administration, counting specimens by means of a Geiger–Müller end window tube.[4] Recently, measurements of exchangeable potassium have been made using Geiger–Müller liquid counters to measure urine activity 24 hr after administration of 50 μc of K^{42} to human beings.[5] Geiger–Müller dip counters were used[2] to count serum obtained 24 hr after administration of 350 μc of K^{42}.

Thin-walled plastic well scintillation counters have been described and have been shown to have high sensitivity for counting energetic β-particles in liquid samples.[6,7] These were shown to have high efficiency for

K^{42} in liquid samples up to 4 ml in volume.

It is the purpose of this paper to describe plastic well counters similar to those described by HINE *et al.*[6] and MICHEL *et al.*,[7] but of greatly increased sensitivity which is largely a result of the large volumes of liquid sample with which they may be used. The use of these counters in making measurements of exchangeable potassium in man is also described and discussed.

SCINTILLATORS AND DETECTORS

The thin plastic well scintillators which have been described by the authors cited have had wall thicknesses of from 0·318 cm to 0·477 cm. They have been designed to accept commercial plastic test-tubes* of 20 ml capacity. The heights of these scintillators were 4·44 cm, which limited sample size to 4 ml maximum.

The need for optimum counting sensitivity in measurements of exchangeable potassium

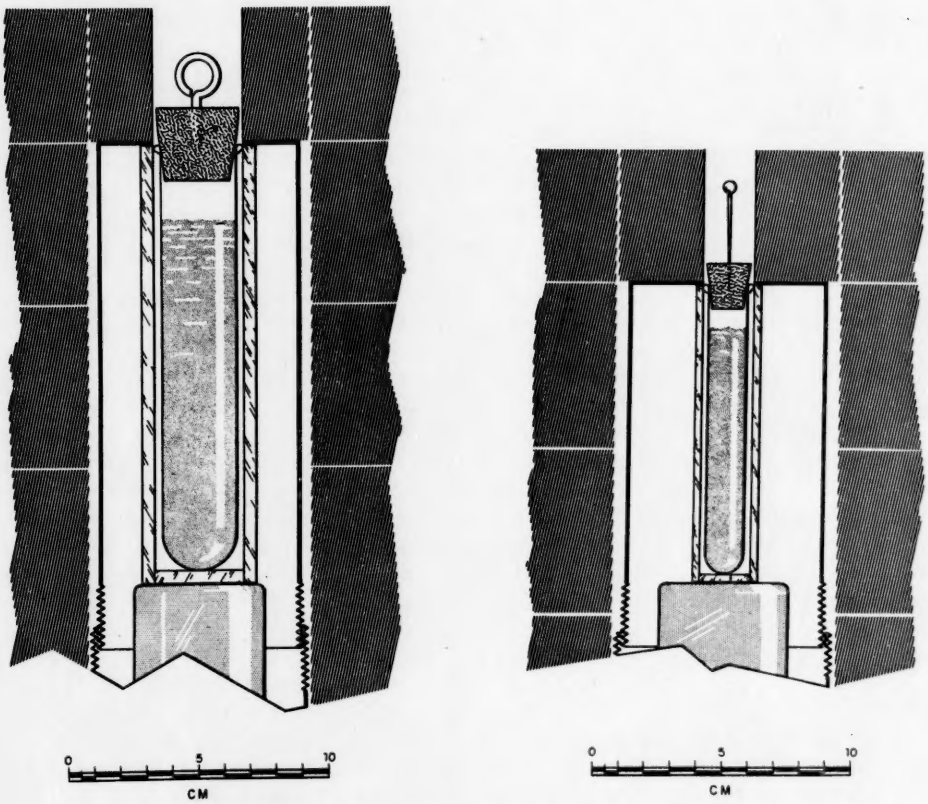

FIG. 1. The 20 ml and the 100 ml scintillators are shown mounted on the 2 in. photomultiplier with which both were used. Their relations to the aluminum sleeve, the lead shielding, and the plastic sample tube are shown.

* Lusteroid, International Equipment Co., Boston, Massachusetts.

led us to experiment with well scintillators of this type, modified so that larger sample volumes could be used. A well scintillator was made of the same commercial scintillating plastic* used by the authors cited. This had a tubular wall 0·318 cm thick and 6·98 cm high, with 1·90 cm bore. A disc of plastic phosphor, 1·90 cm in diameter by 0·318 cm thick, formed the well bottom. Both pieces of the scintillator were brightly polished after machining, in order to ensure optimum light piping within the scintillator. This scintillator will be referred to as the prototype scintillator. Silicone grease was used as a coupling medium. The scintillator was held pressed against the spring-loaded 2 in. photo-multiplier by means of a flanged aluminum tube. The photomultiplier was used with a preamplifier and scaler. From tests done using this assembly, it appeared (see results) that two other scintillators should be made. These were:

(1) a well scintillator to accept the same (20 ml) plastic test-tubes used with the prototype, but to have the same height as these test-tubes, and
(2) a well scintillator to accept 100 ml plastic test-tubes,† and to have the same height as those tubes.

These will be referred to as the 20 ml scintillator and the 100 ml scintillator, respectively. The 20 ml scintillator had a tubular wall 0·318 cm thick and 11·11 cm high. The bore was 1·90 cm. The well bottom consisted of a disc of scintillating plastic 1·90 cm in diameter and 0·318 cm thick. The 100 ml scintillator had a tubular wall 0·477 cm thick and 16·19 cm high. The bore was 3·60 cm. A disc of plastic phosphor 0·477 cm thick and 3·60 cm in diameter formed the well bottom.

These two scintillators were used in conjunction with the same 2 in. photomultiplier, amplifier, and scaler mentioned above. As before, all pieces of the scintillators were brightly polished prior to assembly. The relationships of the 20 ml scintillator and the 100 ml scintillator to photomultiplier, samples, and shielding are shown (Fig. 1).

Shielding and housing

Two inches of lead shielding were placed on bottom, sides and top of the scintillator–detector unit. For optimum β-detection, the transparent scintillators were exposed directly to the sample tubes. Accordingly, a light-tight enclosure was needed. One was designed which allowed quick sample changing, yet protected the photomultiplier tube from damage due to accidental exposure to room light while supplied with high voltage. A diagram of this housing is shown (Fig. 2). Background counting rates were: prototype well 40 counts per min, 20 ml well 80 counts per min, and 100 ml well 150 counts per min.

Counter efficiency

Since this type of counter is useful for counting any isotope which emits energetic β-particles, tests were performed using both K^{42} and P^{32} as sources.

To test the prototype phosphor, successive 1·0 ml volumes of both a K^{42} solution and a P^{32} solution were added in turn to different counting tubes, and counting rates were taken after each addition of radioactive sample. The counting rate rose with both K^{42} and P^{32} in linear fashion until the fluid in the tubes became level with the top of the phosphor. This occurred when each plastic tube contained about 11 ml of liquid sample. Additions of sample beyond 11 ml produced little further increase in counting rate.

To test the 20 ml and the 100 ml phosphors, a K^{42} and a P^{32} solution were prepared each having activity of about 20,000 counts per min in 10 ml volumes, when these were placed in 100 ml plastic test-tubes and counted in the 100 ml well. The number of disintegrations per min per ml of volume was determined for each of these two solutions by means of a calibrated proportional

* Scintillator B, Pilot Chemicals, Inc., Watertown, Massachusetts.
† Lusteroid, International Equipment Co., Boston, Massachusetts.

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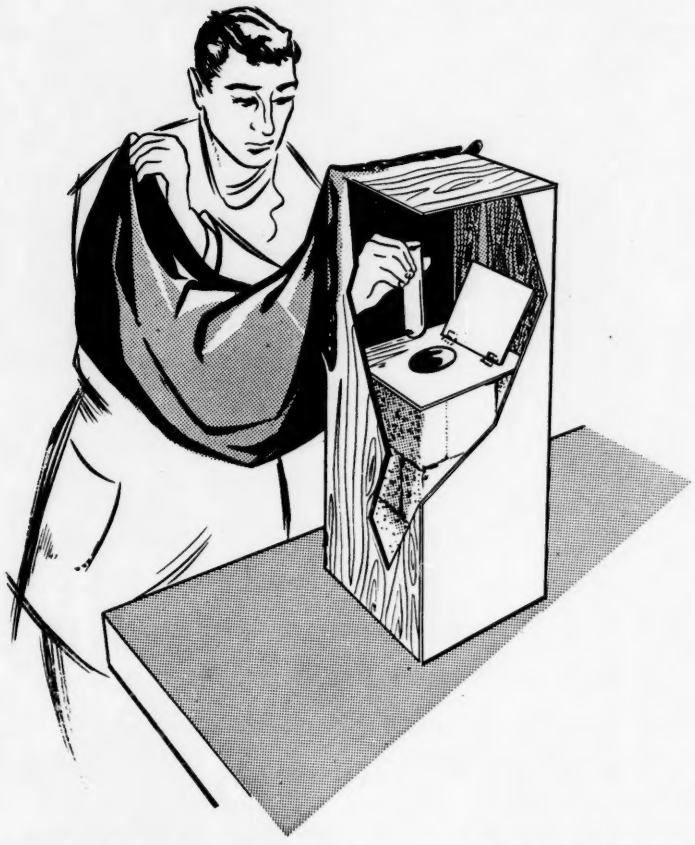

FIG. 2. A schematic drawing shows the way in which the light-tight box prevents light from entering the photomultiplier during changing of samples.

flow counter. These disintegration rates were later used to calculate counting efficiency for the two well counters for the different isotopes and sample volumes.

With the 20 ml phosphor in place, the two solutions were counted using sample volumes of 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18 ml, by adding successive aliquots of sample to plastic test-tubes, and counting each tube after each addition. In similar fashion, with the 100 ml well in place, these same two solutions were counted using sample volumes of 10, 20, 30, 40, 50, 60, 70, 80 and 90 ml. The counting rates were corrected for background and for radioactive decay. No coincidence corrections were necessary, since dilution curves showed that a linear response was obtained over the range (0–105,000 counts per min) used.

The efficiency of counting for K^{42} and P^{32} at each sample volume was then computed using the data from the calibrated proportional flow counter, by means of the expression

$$\text{Efficiency} = \frac{\text{counts per min of sample}}{\text{disintegrations per min per ml} \times \text{sample volume (ml)}}$$

The data are shown (Table 1).

Discussion of counter characteristics

From Table 1 it may be seen that counting rate increases steadily, with both isotopes counted in both well phosphors, as the

TABLE 1. Counting rate and efficiency as functions of sample volume

Counter	Sample volume (ml)	counts/min K^{42}	$\frac{\text{counts/min}}{\text{disinteg./min}}$	counts/min P^{32}	$\frac{\text{counts/min}}{\text{disinteg./min}}$
20 ml well	1	3895	0·494	4244	0·203
	2	6335	0·402	6050	0·145
	4	10,680	0·339	9857	0·118
	6	14,720	0·311	13,370	0·107
	8	18,920	0·300	17,023	0·102
	10	23,570	0·299	20,649	0·099
	12	27,240	0·288	24,130	0·096
	14	30,980	0·281	28,130	0·096
	16	35,780	0·284	31,550	0·094
	18	40,420	0·285	34,850	0·093
100 ml well	10	20,720	0·263	20,814	0·100
	20	32,100	0·204	31,080	0·074
	30	43,000	0·182	38,951	0·062
	40	54,160	0·172	47,571	0·057
	50	63,240	0·160	56,048	0·054
	60	75,000	0·159	63,809	0·051
	70	85,360	0·155	72,587	0·050
	80	94,720	0·150	81,769	0·049
	90	104,800	0·148	89,435	0·048

volume of radioactive solution increases. The increases in counting rate continue until the sample tubes are full. The rate of increase per volume of sample is greater in the 20 ml well than in the 100 ml well. The counting rates at sample volumes of 18 ml are about four times those at volumes of 4 ml. The counting rates at sample volumes of 90 ml are about two and one-half times those at sample volumes of 18 ml, and about ten times those at sample volumes of 4 ml. When one is using a sample which is easily obtained in volumes up to 90 ml, it is seen that one will have either a ten-fold increase in counting rate, or a ten-fold reduction in the dose of isotope needed, when counting samples of 90 ml volume rather than samples of 4 ml volume.

From Table 1 it may also be seen that as sample volumes are increased, there is with each isotope a sharp initial drop in counting efficiency. As further additions of sample are made, however, efficiency drops much more slowly. Thus, for K^{42}, the efficiency is 20 per cent at volumes of 20 ml, and 15 per cent at volumes of 90 ml. This is associated with the worthwhile increases in counter sensitivity which are achieved by increasing the sample volume. It can also be seen from these data that these counters are quite useful for counting low activity P^{32} solutions. The efficiency for P^{32} at sample volumes of 90 ml is 5 per cent. The counting rate of such a sample would be the same as that of a 9 ml sample counted at a hypothetical efficiency of 50 per cent.

Surface area: counting rate relationships

Although the counting rates of samples of a given K^{42} or P^{32} solution rise as the sample volume is increased, the rate of increment differs from the 20 ml to the 100ml well. These counting rates can be shown to bear close relationship to the surface areas of the liquid samples being counted. The physical dimensions of each volume of sample used in taking the data shown in Table 1 were carefully measured. The surface areas of bottom, sides and top of the samples in the tubes were computed. The areas of the top

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surfaces of the samples were reduced in each case by a proportion which allowed for the angle subtended at a point in the center of the top surface by the diameter of the hole at the top of the scintillator. This allowed for those β-particles which might escape without having a chance to contact the scintillator. No corrections were made for β-absorption by air or by the 62 mg/cm^2 celluloid walls of the test-tubes. The counting rate of each sample is related to the surface area of the sample (Fig. 3). It is seen that the counting rate of an aliquot of a given solution of K^{42} or P^{32} is closely related to the surface area of the liquid sample being used, when counted in either the 20 ml or the 100 ml well.

Specific gravity of the sample

With these counters, the specific gravity of the solutions used exerts an effect upon counting efficiency. Solutions of K^{42} with sucrose having known activity, and specific gravity ranging from 1·000 to 1·050 were prepared. These were counted to 1 per cent statistics in quadruplicate. The results showed that solutions of K^{42} lying within this specific gravity range could be corrected to water equivalent by means of the formula:

$$\text{corrected counts per min} = \text{observed counts per min} \times [1 + (\eta - 1)0{\cdot}8]$$

in solutions of specific gravity η.

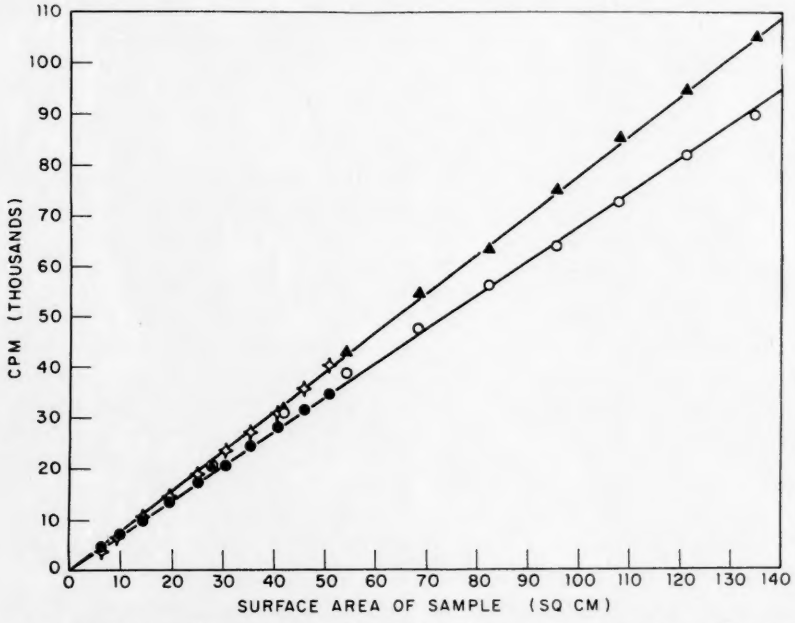

FIG. 3. The counting rate of a solution of K^{42} is shown as a function of the surface area of the liquid sample in the test-tube. Both the 20 ml and the 100 ml wells fall on the same line, which passes through zero. The same comparison is shown for P^{32}.

APPLICATION OF THESE COUNTERS IN MEASUREMENT OF EXCHANGEABLE POTASSIUM IN MAN

The 100 ml phosphor is used for measurement of exchangeable potassium in man. Equilibrium periods of 40 hr are used. Urine samples taken 40 hr after administration of 50 μc of K^{42} give counting rates which usually range from 1000 to 2000 counts

TABLE 2. Equilibration of K^{42} in a healthy man

Sample number	Time of voiding (hr)	Counts minus background counts/min per 80 ml	Counts at 40 hr counts/min per 80 ml	Potassium concentration m. equiv./l	Urine volume (ml)	Specific activity counts/min per m. equiv.	Exchangeable potassium m. equiv.
1	2°0′	2500	2754	35·5	115	937·4	
2	5°30′	2702	3145	73·2	144	519·1	
3	15°40′	1395	1777	56·4	243	380·7	
4	20°20′	739·9	977·5	34·6	345	341·3	
5	23°55′	365·2	501·3	18·2	355	331·9	
6	30°30′	486·2	691·1	25·3	387	330·1	
7	40°0′	829·0	1209	46·4	208	314·9	4260
8	47°0′	1079	1582	59·3	276	322·2	4150
9	54°20′	725·5	3099	117·8	168	317·9	4190
10	64°0′	327·3	1697	73·7	155	321·8	4120
							mean = 4180
							σ = 63

per min per 80 ml of urine. Specific activities are usually about 300 counts per min per m. equiv. of potassium. Five minute counting periods are sufficient. Variations in geometry due to differences in the shapes of the plastic test-tubes are occasionally seen. However, when samples are counted in quadruplicate, the reproducibility of the means is quite satisfactory.

Data taken during the mixing of 50 μc of K^{42} in the exchangeable potassium of a 77·3 kg healthy man are shown (Table 2). During this time the subject was maintained on a diet containing less than 10 m. equiv. of potassium per day. For each urine sample, the time of voiding, actual counting rate of 80 ml of the urine (counts minus background), corrected counting rate (corrected to 40 hr post-injection), potassium concentration, and specific activity are given. It is seen that it was still possible to count the urine specimen which was voided 64 hr after tracer administration, and that specific activity remained essentially constant after the lapse of 40 hr. The four urine samples voided after 40 hr gave values for exchangeable potassium which were in close agreement.

SUMMARY

Plastic well counters of increased sensitivity are described. These are patterned after the counters described by HINE *et al.* and MICHEL *et al.* but have a greatly increased volume capacity. A ten-fold increase in counter sensitivity is achieved. The use of such counters in measuring the exchangeable potassium by means of K^{42} dilution is described. Data are given showing the mixing of 50 μc of K^{42} in the exchangeable potassium pool of a healthy man, measured with these counters. Data are given up to 64 hr after isotope administration, at which time counting rate was 300 counts per min above a background rate of 150 counts per min. Counting rates of 80 ml aliquots of urines voided 40 hr after administration of 50 μc of K^{42} to adult men usually are between 1000 counts and 2000 counts per min.

Acknowledgements—I would like to express my appreciation to Captain A. R. BEHNKE, Dr. ROBERT R. NEWELL, Dr. CECIL ENTENMAN, Dr. EDWARD ALPEN, and Mr. ARTHUR H. REDMOND for their kind advice and co-operation.

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technical notes

The Superposition of Autoradiographs and Micrographs using the Kodak Dye Transfer Process

(*Received* 19 *February* 1959)

A MICROGRAPH from a transparent specimen which has been autoradiographed using the stripping film technique[1] shows the distribution of radioactive tracer superposed on the microstructure. The stripping film technique is not satisfactory for opaque and especially for metallic specimens[2] and therefore the autoradiograph and micrograph must be obtained separately. It is much easier to interpret the autoradiograph when the distribution of radiotracer is superposed on the microstructure.

In the Kodak Dye Transfer Process[3] coloured images, obtained from separation negatives, are superposed to produce a coloured print. This process can be used to make a composite print showing the autoradiograph and micrograph in appropriate colours by using the autoradiograph and micrograph in place of separation negatives. Such composite prints are much more easily interpreted than separate or superposed black and white prints.

Figs. 1 and 2 show examples of composite prints obtained by this method where the colours were obtained by transferring cyan and yellow micrograph dye images and magenta and yellow autoradiograph dye images.

In Fig. 1 an autoradiograph obtained using copper-64 as a radio-tracer shows the distribution of copper in an aluminium 4% copper alloy cooled from the melt at 0·35°C/min. Micrographs ×36·5 of the specimen, etched in aqueous 25% HNO_3 + 2%HF, and of the autoradiograph, were contact printed on to separate matrix films. Both matrices were processed and registered according to the manufacturer's instructions. The matrices were dyed to give a suitable combination of colours and the dye images transferred to paper in the usual way. Regions of the alloy containing copper, i.e. those which were radioactive, are shown in red and dark etching regions of the micrograph in green; hence regions which contain copper and etch dark appear black.

Fig. 2 shows the distribution of chromium in an aluminium 5½% Zn, 2½% Mg, 0·2% Cr alloy after homogenization at 460°C for 25 hr. Micrographs ×7·8 of the autoradiograph and of the specimen etched in Keller's reagent, were enlarged ×3·1 on to matrix films which were processed as for Fig. 1. Regions of the alloy containing chromium are shown in red; dark etching regions of the micrograph and holes in the specimen in green, hence regions which contain chromium and etch dark appear black.

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3. Kodak Data Sheets CL 1, 2.

Investigation of the Characteristics of a Sedimentation Tank by a Radioactive Tracer Technique

(*Received* 24 *December* 1958;
in revised form 23 *February* 1959)

A RADIOACTIVE tracer experiment was made to determine the throughput time and dispersion of a sample of water passing through a radial flow sedimentation tank in the Bridge of Earn sewage purification works. The tank has a capacity of 50,000 gal and discharges into a tidal river not used as a source of drinking water. Before the experiment, the mean throughput time was estimated to be about 12 hr.

Na^{24} was chosen as a tracer, to avoid long-lived radioactive contamination. The activity used was 100 mc to provide ultimate concentrations well below the maximum permissible level for drinking water (8×10^{-3} μc/ml)[1] even though the effluent was not into a potable water supply.

The tracer was introduced in the form of sodium bicarbonate (1·5 g) dissolved in 100 ml of dilute hydrochloric acid. After the removal of 0·25 ml of solution for comparison purposes, the remainder was poured into the inlet channel of the tank, just above the standing wave flume.

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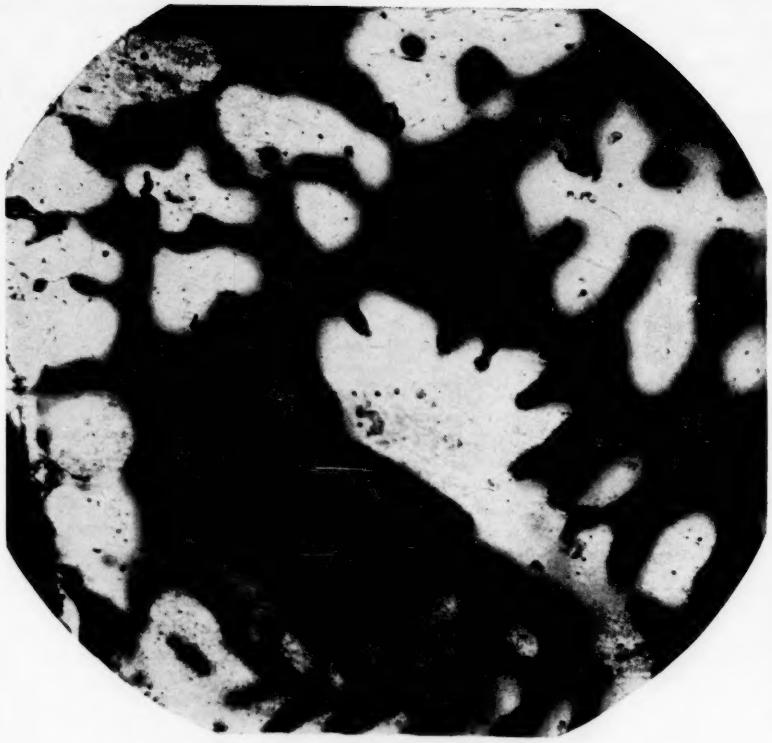

FIG. 1. Superposition of a micrograph (green) and an autoradiograph (red) showing copper in a copper–aluminium alloy. ×36·5.

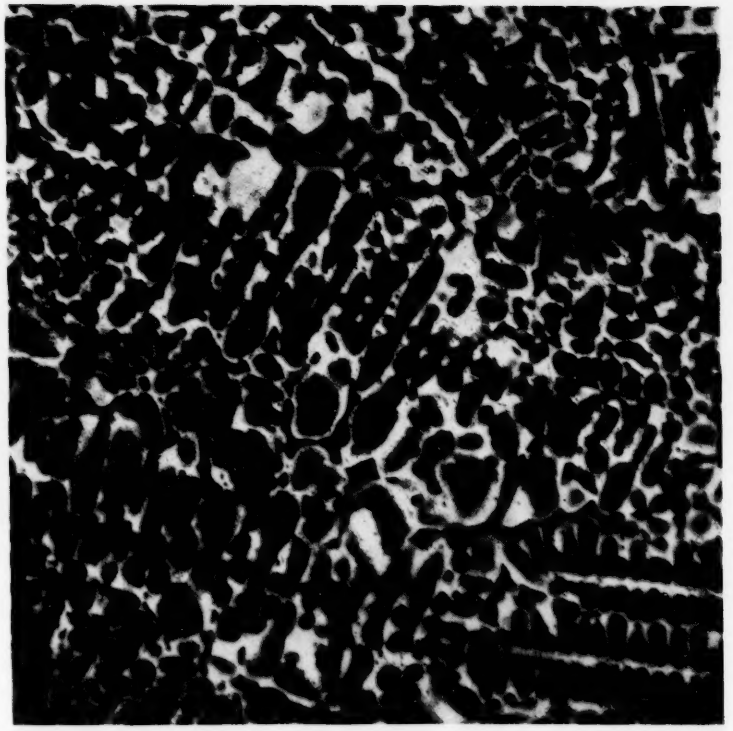

FIG. 2. Superposition of a micrograph (green) and an autoradiograph (red) showing chromium in an aluminium–zinc–magnesium alloy. ×24·4.

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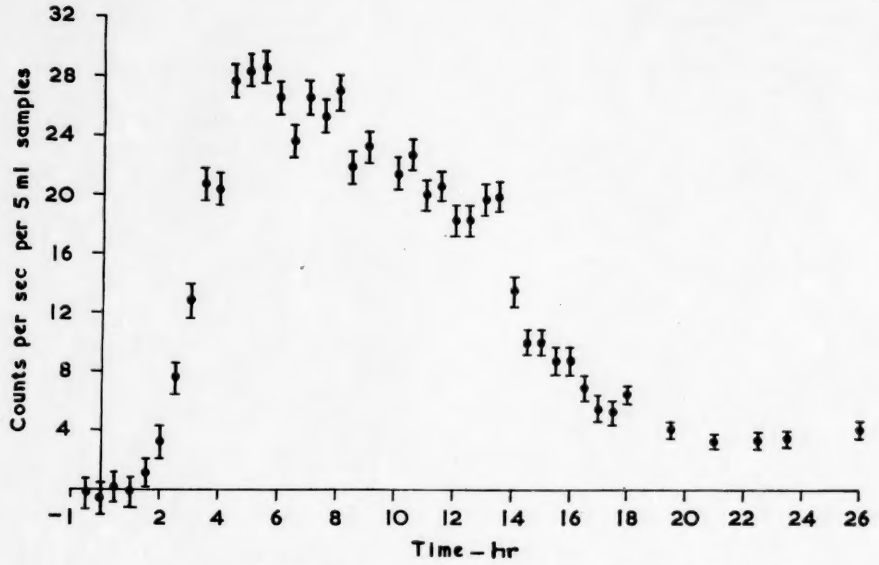

FIG. 1. Effluent sample counting rate as a function of time after insertion of the radioactive solution.

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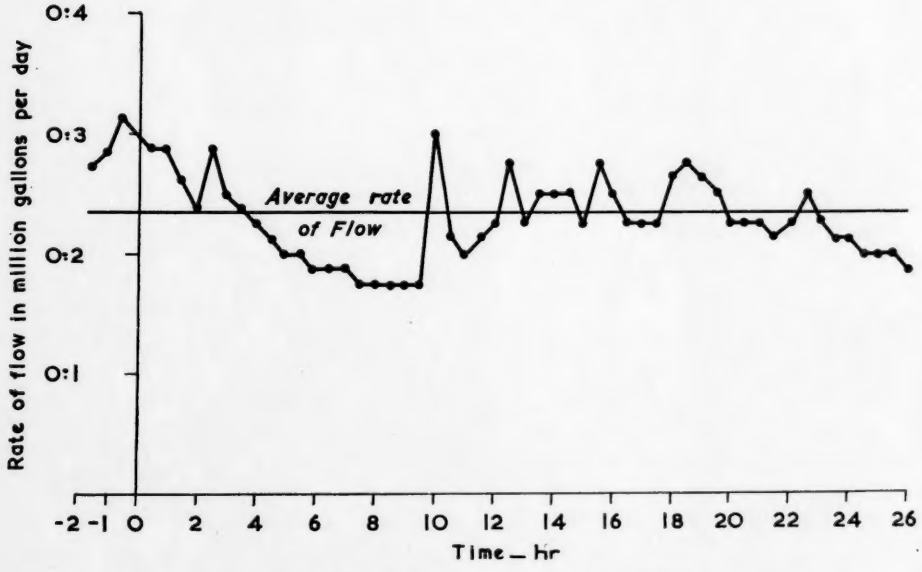

FIG. 2. Rate of flow of sewage into the tank throughout the experiment.

From the discharge point of the circumferential channel, 5 ml samples of liquid were taken at intervals of half-an-hour after the injection and measured in a well-type scintillation counter. Fig. 1 shows the counting rates obtained as a function of time; vertical lines indicate the standard deviation. The rate of flow into the tank during the period of the experiment was recorded by the standing wave flume recorder. Readings at half-hour intervals are shown in Fig. 2.

from the tank, will depend on how quickly changes in the inflow are reflected as changes in the outflow—in fact on the integrating time constant of the settling tank. Fig. 1 represents the curve obtained assuming a very long time constant and Fig. 3 that with a time constant of zero. The measurements of the variations of the rate of flow were made at the inlet channel and, as a large tank would produce a great smoothing effect, the flow from the discharge point was probably

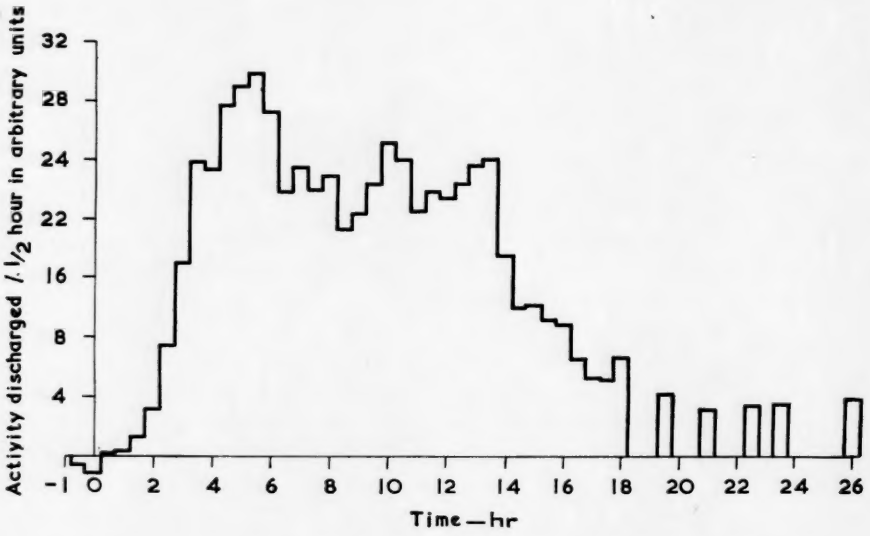

FIG. 3. The activity discharged from the tank as a function of time after insertion of the radioactive solution.

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Discussion of results

From Fig. 1 it can be seen that none of the inserted material appeared at the discharge point of the circumferential channel until about 2 hr had elapsed from the time of insertion. Most of the radioactive solution was clear of the tank after about 14 hr, but a small residuum appeared to be leaking out very slowly.

Fig. 1 does not give a completely accurate picture of the rate of output of radioactive material, because it does not take into account variations in the rate of flow of sewage through the tank. A histogram showing the total activity discharged in each half-hour period was constructed, from Figs. 1 and 2, and is shown in Fig. 3. The ordinate of Fig. 3 is in arbitrary units but the standard errors, although not plotted, are of the same order of magnitude as those shown in Fig. 1. The true curve for activity discharged almost constant during the course of the experiment. In the conditions of this experiment Fig. 1 is therefore likely to be nearer the true curve than Fig. 3. Fig. 1 has a typical shape for a flow curve accompanied by dispersion, and indicates that good mixing is occurring.

Acknowledgements—The authors would like to thank Mr. J. McL. FRASER of Babtie, Shaw & Morton, Consulting Civil Engineers, Glasgow, for much helpful advice on the civil engineering aspects of the problem. Mr. J. C. LAW and other members of the staff of Perth County Council kindly provided the help needed on the site.

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Reference

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A Portable Radioactive Solution Container*

(*Received* 13 *October* 1958)

Introduction

THE use of glass to contain radioisotope solutions characterized by penetrating beta and gamma emission often directly presents problems of external irradiation hazard to the experimenter. The quantity and concentration of the radioisotope stringently limits the experimental working time. The consequent need for perhaps hurried and often inconvenient manipulation of a fragile container of unshielded radioactive solution may hinder removal of aliquots or facilitate breakage of the container with loss of control of the radioactive solution. A portable lead shielded container which minimizes or eliminates these hazards and avoids the bulk of mechanically controlled dispensers[1] has been designed in this laboratory.

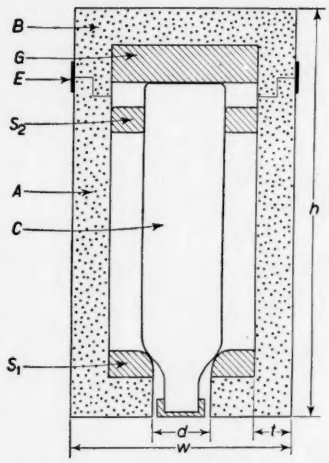

FIG. 1. Schematic diagram of portable radioactive solution container.

Materials and methods

The device illustrated (Fig. 1) may be constructed from materials readily available in radioisotope laboratories. It consists of a cylindrical flat-ended lead pig *A* of dimensions *h*, *w*, and *t* with removable cap *B*, modified to accommodate a serum bottle *C* which contains radioisotope solution. The serum bottle is supported within the lead container by means of rubber sleeves S_1 and S_2 and a solid rubber gasket *G*. These may be conveniently formed from rubber stoppers. A circular hole of diameter *d*, drilled in the base of the container opposite the cap, accommodates the neck of the serum bottle. To ensure that the serum bottle is held securely within the lead container when the cap is positioned, rubber gasket *G* is inserted in the recess of the lead cap in direct contact with the serum bottle. The thickness of this gasket is such that a slight positive pressure is transmitted through the neck of the serum bottle to sleeve S_1 when the lead cap is sealed on with a band of adhesive masking tape *E*. The size of the glass serum bottle to be employed and the nature of radioisotopes will determine dimensions of the solution shield components. The suggested dimensions shown in Table 1 are for use with both 5 and 10 ml serum bottles.

TABLE 1. Suggested dimensions of portable radioactive solution container

Dimensions (cm)				Radioisotope
h	*w*	*d*	*t*	
8·5	3·4	1·4	0·32	P^{32}, Y^{90}
9·8	4·6	1·4	1·27	Zn^{65}, Cs^{137}

Exposure to radiation during readying of the apparatus for use with radioactive solutions can be minimized by the following suggested procedure. Sleeve S_1 is positioned. Sleeve S_2 is medially placed on the *empty* uncapped serum bottle. The serum bottle is then positioned in the lead container and the radioisotope solution added remotely or from a shielded hypodermic syringe. The serum bottle is capped and the lead container cap containing gasket *G*, is emplaced and sealed to the body of the shield. Aliquots of the solution may be removed as desired by means of an appropriate shielded hypodermic syringe and needle, although some precaution must be taken to avoid exposure to radiations emitted through the small exposed portion of serum bottle and rubber cap at the base outlet. Following use with radioactive solutions any residual contamination of the lead container may be removed chemically or by excision of the contaminated metal. The excised portion may be rebuilt with lead scrap.

* This work was performed under contract No. W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company.

Summary

The portable lead solution container conveniently permits safe and convenient handling and transfer of radioactive solutions with minimal hazard. Its relatively light weight permits it to be manually moved or maintained in any position by use of only a clamp and a fixed ring stand. It excludes container breakage and gross contamination of working areas, and without exceeding permissible radiation exposure limits, obviates to a great extent remote handling of millicurie amounts of radioisotopes.

Acknowledgement—The author is pleased to acknowledge the technical assistance of S. WILSON, Irradiation Processing Department.

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Reference

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book reviews

H. R. Beck, H. Dresel und H. J. Melching: **Leitfaden des Strahlenschutzes für Naturwissenschaftler, Techniker und Mediziner.** Georg Thieme Verlag, Stuttgart, 1959. 253 Ss, Preis unbekannt.

Der über 250 Seiten starke Leitfaden hat stellenweise eher den Charakter eines Lehrbuches. In klarer und einfacher Form werden die Grundbegriffe der Strahlenphysik, des Atombaus, der Masseinheiten, der Strahlenbiologie etc. erläutert. Die einzelnen Kapitel werden jeweils mit einer Schrifttumsübersicht beschlossen. Damit kann die vorliegende Form sicher für Studienzwecke empfohlen werden. Der am Schluss angefügte Organisationsplan für den Kriegsfall lässt allerdings vermuten, dass der Leitfaden doch einem wesentlich grösseren Kreis von Interessenten dienen sollte. Wenn man davon absieht, dass nach den vorhergehenden Ausführungen auch der Laie unschwer erkennen kann, dass eine Schutzmöglichkeit in einem derartigen Fall nicht existiert, wäre für den praktischen Gebrauch zu überlegen, ob eine Aufteilung in einen theoretischen und einen praktischen Teil zur schnelleren Orientierung nicht ratsamer wäre. Der praktische Teil könnte dann bequem auf etwa 40–50 Seiten reduziert werden. Dabei könnten gleichzeitig einige missverständliche Bezeichnungen leicht vermieden werden. z.B. könnte die Bezeichnung der Ordinate in der Zeichnung auf Seite 187 vermuten lassen, dass es sich um wirkliche "Aktivitäten" handelt. Auf Seite 193 ist das Verbot der Ausführung nicht radioaktiver Arbeiten an aktiven Arbeitsplätzen durch die zu fordernde Trennung aktiver und inaktiver Arbeitsräume überflüssig. Auf Seite 201/202 könnten die 10 Gebote der Arbeitstechnik bequem durch eine Forderung nach strengster Arbeitsdisziplin ersetzt und ergänzt werden, die u.a. bei jedem Tätigkeitswechsel Waschen und Messen der Hände als selbstverständlich erachtet. Unter diesen Umständen könnte bei konsequenter Durchführung selbst das Rauchen etc. gestattet werden.

F. Strassmann

Glenn T. Seaborg: **The Transuranium Elements.** Academic Books, London, 1958. 354 pp. 56s.

Since the discovery of element 93 (now called neptunium) in 1940, nine more elements beyond uranium have been synthesized. The most important of these is, of course, plutonium, number 94, and the large scale production of this element occupied a large part of the war-time nuclear energy effort in the U.S.A. Professor Seaborg has been a leading figure in the chemical side of nuclear energy research since its beginnings, and he is a co-discoverer of most of the new elements. He shared the Nobel Prize for Chemistry in 1951.

The present volume was prepared especially for the 1958 Geneva Conference. It consists of four chapters, based on lectures given by the author at Yale during 1957. They are entitled respectively "The Plutonium Story", "Chemical Properties of the Actinide Elements", "Nuclear Properties of the Transuranium Elements", and "Future Synthetic Elements". A surprising feature of the book is the wide diversity of style and approach from one chapter to another, and even from one page to another. For instance, after discussion of hybrid orbitals on page 148, we come on page 158 to a light-hearted correspondence with the *New Yorker* magazine on the naming of new elements.

Although much of the early chemical work has been published piecemeal during the past 10 years, Professor Seaborg's "Plutonium Story" is the first connected account (the subject was dismissed briefly in the 1946 Smythe Report). It occupies more than one-third of the volume, and is written in a popular style with many anecdotes, and personal reminiscences. The development of the kilogram-scale industrial process from microgram-scale chemical experiments seems even today an almost unbelievable achievement, especially when it is remembered that the whole project was accomplished in a little over 3 years. The detailed charts of personnel and organization may seem tedious, but the author's desire to acknowledge all his war-time colleagues is understandable.

By contrast with these memoirs, the chemical and nuclear chapters make much greater demands on the reader. Indeed, there must be few chemists with sufficient knowledge of nuclear physics to follow the whole of the third chapter (Professor Seaborg himself acknowledges instruction on the Unified Nuclear Model). However, these chapters do provide a useful summary of the present state of knowledge.

In the last chapter, the author predicts the nuclear and chemical properties of elements beyond number 102. While he admits that this is written in a fanciful vein, no one is better qualified to indulge in such speculation.

J. Milsted

Gloved Boxes and Shielded Cells for Handling Radioactive Materials. Edited by G. N. WALTON (Chairman, Editorial Board). Butterworths, London. Academic Press, New York, 1958. xii + 515 pp. 95s. $16.80.

THE opening pages of this book present an excellent discussion of the philosophy of "control through confinement", providing justification for the use of enclosures of the Gloved Box type for work with radioactivity. A comprehension of this philosophy is essential if one is to readily grasp the significance of the special designs incorporated in the equipment and techniques described throughout the book. The philosophy may be considered as made up of the basic features which must necessarily be provided to achieve safety, efficiency and economy in dealing with radioisotopes.

The many authors have presented views and experience with the component materials and parts of enclosures and described their performance under special applications. In most articles the details of specifications and construction for gloved boxes are combined with generalized comments as a help to anyone adapting design features to new problems.

It is unfortunate that the preponderance of material is drawn from plutonium activities, since there is a large number of valuable applications of gloved boxes in industries, hospitals, universities, and research institutions dealing with a variety of radioisotopes.

The titles of the papers provide a convenient summary of the most important considerations in the design of enclosures and thus become an easy reference for viewing systems, shielding, decontamination, ventilation, filtration, criticality, gloves, manipulators, etc.

The technical features are quite well covered in each paper and the many illustrations are exceedingly valuable, but the economic factors are loosely mentioned. The efficient application of the enclosure philosophy frequently results in substantial savings as a "by-product" but these are referred to largely by inference.

A study of the developments described in this book would be essential for anyone contemplating the processing of plutonium, especially within the United Kingdom, since the commercial sources of applicable materials and equipment for that region are listed.

N. B. GARDEN

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international news

U.S.A.

Industrial Radioisotope Meetings

THE U.S. Atomic Energy Commission has co-sponsored a series of technical symposia and workshops on the industrial applications of radioisotopes at Miami, Florida; Manhattan, Kansas; and Atlanta, Georgia. Current planning is under way to hold an industrial radioisotope symposium at San Francisco, California, in December, 1959.

Educational Assistance

THE U.S. Atomic Energy Commission recently announced the establishment of a new program of assistance to colleges and universities for education and training in radioisotope principles and technology. Specifically, the program provides for financial grants for laboratory equipment and required demonstration apparatus. To date, grants have been awarded to thirteen colleges and universities under this program.

Michigan Nucleonic Society

THE Michigan Nucleonic Society has been formally organized in a general meeting held on 11 March, 1959 at the University of Michigan. The Society has been active for the last 2 years under the name of the Nucleonic Discussion Group.

The object is to promote the exchange of scientific information and liaison between workers in nuclear science. Membership is open to all interested in work with radioisotopes, radiation and allied fields. Officers are: *Board of Directors:* A. EMMONS, DOUGLAS COOPER, GORDON NOAKES, RICHARD HAHN, J. J. GUMBLETON. *Secretary:* ARTHUR SOLARI. *Vice-chairmen:* RICHARD ABOWD. *Chairman:* LUTHER PREUSS. For information write to the secretary, 509 Linden Street, Ann Arbor, Michigan.

Third Industrial Nuclear Technology Conference

THE Third Industrial Nuclear Technology Conference is to be held on 22, 23 and 24 September, 1959 at the Morrison Hotel, Chicago, Illinois. The conference is co-sponsored by Armour Research Foundation and *Nucleonics* magazine in co-operation with the U.S. Atomic Energy Commission.

The conference will discuss radiation effects; source design, nuclear instrumentation, activation analysis, isotope production, tracer studies and radiation processing. Papers to be presented will contain the latest results of research in industrial and government laboratories both in the U.S.A. and abroad. Reports on progress of many of the programs sponsored by the USAEC Office of Industrial Development will be included in the well-rounded technical program. A detailed program will be published well in advance of the conference.

For further information, contact L. REIFFEL, Co-chairman Armour Research Foundation Technology Center, Chicago 16, Illinois.

AUSTRIA

Fourth International Symposium on "Radioactive Isotopes in Clinical Medicine and Research"

THE Fourth International Symposium on "Radioactive Isotopes in Clinical Medicine and Research" will take place in Bad Gastein, Austria, 7–10 January, 1960.

The topics selected for discussion will be:

(1) Calcium and strontium isotopes in the study of calcium metabolism and the localization of bone tumors.

(2) Peripheral metabolism of thyroid hormones and iodinated amino acids.

(3) Radioisotopes in the study of glucose and insulin metabolism in normal and diabetic patients.

(4) Estimation of total body and extracellular water.

(5) Estimation of body content and turnover of Electrolytes.

(6) Studies of red cell sequestration by *in vivo* counting.

(7) Estimation of organ blood flow using inert gas techniques.

(8) New developments in radioisotope therapy.

The official languages will be English, French and German. Those who wish to present papers should submit abstracts before the end of June 1959 to Dr. R. HÖFER, Radioisotopes Laboratory, 2nd Medical University Clinic, Garnisongasse 13, Vienna 9, Austria, who will be pleased to give further detailed information.

forthcoming papers

Z. K. Maizus, L. G. Privalova and N. M. Emanuel: Use of the kinetic tracer method for investigations on the mechanism of *n*-decane liquid-phase oxidation.

S. M. Makin and A. E. Nunley: An autoradiographic method for determining the distribution of iron on recording tape.

Milton G. Crane, John E. Holloway, Charles Sears, James McCeachen and Ralph Adams: The effect of recirculation on the shape of the arterial concentration curve after an instantaneous injection of indicator.

A. M. Brodsky, R. A. Kalinenko and K. P. Lavrovsky: On the kinetic isotope effect in cracking.

M. Anbar, S. Guttmann and Z. Lewitus: The mode of action of perchlorate ions on the iodine uptake of the thyroid gland.

G. A. Ovezall-Klaasen and J. Halberstadt: The preparation of S^{35} and/or Cl^{36}-labelled SO_2Cl_2.

D. J. Chleck and C. A. Ziegler: The preparation and some properties of radioactive quinol krypton clathrate compounds.

R. M. Black and A. Charlesby: The oxidation of irradiated polyethylene–I. Radio-oxidation–II. Thermal oxidation.

I. P. Alimarin and G. N. Bilimovitch: The isotope dilution method and its application to analysis of inorganic substances.

M. Laine-Böszörmenyi et P. Fallot: Étude de l'absorption digestive de l'eau chez les malades atteints de cirrhose du foie à l'aide de deux indicateurs de l'hydrogène.

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